



**NON-ADIABATIC ENERGY SURFACES OF  
THE B+H<sub>2</sub> SYSTEM**

THESIS

Lachlan T. Belcher, Second Lieutenant, USAF  
AFIT/GAP/ENP/05-01

**DEPARTMENT OF THE AIR FORCE  
AIR UNIVERSITY**

**AIR FORCE INSTITUTE OF TECHNOLOGY**

**Wright-Patterson Air Force Base, Ohio**

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Lachlan T. Belcher, B.S.

Second Lieutenant, USAF

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Lachlan T. Belcher, B.S.  
Second Lieutenant, USAF

Approved:



David Weeks (Chairman)

7 Mar 05

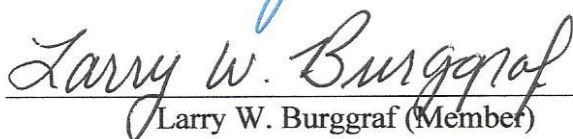
date



William F. Bailey (Member)

7 Mar '05

date



Larry W. Burggraf (Member)

7 Mar '05

date

## Abstract

Generally chemical calculations are made simpler by invoking the *Born-Oppenheimer Approximation*, in which the dynamics of electrons and nuclei are considered separable; this class of chemistry is known as *adiabatic chemistry*. However, in some situations this approximation fails to effectively describe a chemical system; this class of chemistry is known as *non-adiabatic chemistry*. Examples of non-adiabatic chemistry include open-shell reactions with atomic oxygen,  $O+N_2$ , such as might happen in the upper atmosphere. The  $B+H_2$  system, the focus of this thesis, is also one for which non-adiabatic effects are important, and was initially studied for its possible use as a High Energy Density Material (HEDM).

The Hamiltonian operator that describes chemical systems can be split into the sum of kinetic and potential energy operators. In order for the Hamiltonian operator to be useful for creating solvable differential equations for the dynamics of a system, the kinetic energy operator must be diagonal. In the adiabatic representation, the potential energy operator is diagonal, but the kinetic energy operator is not. Chemistry in this representation is only useful when application of the Born-Oppenheimer Approximation allows the assumption that the off-diagonal terms of the kinetic energy operator are negligible. This assumption fails when the off-diagonal terms of the kinetic energy operator, known as *non-adiabatic derivative coupling terms (NAD terms)* become

significant and cannot be neglected. This occurs when the potential energy surfaces of a system come close, touch, or even cross. In order to form useable dynamic equations with the Hamiltonian under these circumstances, it must be represented in a new basis in which the kinetic energy operator is diagonalized. Diagonalization of the kinetic energy operator causes the potential energy operator to become undiagonalized; this form of the Hamiltonian is called the non-adiabatic representation. The coupling angle by which the adiabatic representation is rotated into the diabatic representation is given by a line integral from an arbitrary zero to the configuration in question through the NAD terms. Non-adiabatic chemistry requires a quantum chemistry software package that calculates NAD terms. Computational results from two packages, *Columbus* and *Brooklyn*, are compared and discussed.

Separation of internal dynamics characterized by Jacobi coordinates, and external dynamics characterized by a set of Euler angles and the center of mass position, requires a transformation from Cartesian coordinates, employed by both *Columbus* and *Brooklyn*, to Jacobi coordinates required for subsequent dynamical calculations. Previous attempts to solve for non-adiabatic energy surfaces in this manner have failed because of an ambiguity in selecting the correct variable for describing the overall rotation of the  $\text{B}+\text{H}_2$  system, giving answers that do not agree with specific test cases for which the coupling angle is known via simple symmetry arguments. This error, which lies within the method of converting NAD terms from one coordinate system to another, is discovered and corrected. By way of this correction, correct coupling angles are determined, and non-adiabatic energy surfaces are calculated.

*To my father, who graciously bestowed only upon me the mathematician's gene.*

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I would like to express my thanks to my advisor, Dr. David Weeks, for his driving influence in this thesis. I have learned more about quantum chemistry in the course of this project than I ever could have in the classrooms of AFIT.

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Lachlan T. Belcher



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# NON-ADIABATIC ENERGY SURFACES OF THE B+H<sub>2</sub> SYSTEM

## I. Introduction

### Non-Adiabatic Chemistry

The study of quantum chemistry often takes advantage of a number of approximations, among them the Born-Oppenheimer Approximation. The Born-Oppenheimer Approximation assumes that the difference in mass of nuclei and electrons (the smallest ratio is about 1800:1 for a hydrogen nucleus) causes them to have vastly different timescales, such that the dynamics, and thus the Hamiltonians, of the two groups can be separated. Solution of the electronic Schrödinger wave equation leads to a set of eigenvalues and eigenfunctions, where the eigenvalues serve as potential energy surfaces in the nuclear Hamiltonian. The nuclear Hamiltonian then takes the form of a diagonal potential energy operator and a kinetic energy operator with off-diagonal terms. This form of the Hamiltonian is known as the *adiabatic* representation. A kinetic energy operator with off-diagonal elements does not allow for solvable differential equations for the dynamics of the system. Fortunately these off diagonal elements include derivatives of the electronic wave functions with respect to the nuclear coordinates (called *derivative coupling terms*, or *NAD terms*). Because the Born-Oppenheimer Approximation assumes different electronic and nuclear timescales these derivatives can be approximated to zero,

and both operators can be considered diagonal in this representation. This branch of quantum chemistry is called *adiabatic* chemistry.

For some systems the dynamics of the electrons and nuclei are not so cleanly separable. We may still use the Born-Oppenheimer Approximation to separate the nuclear and electronic Hamiltonians; nevertheless, the derivative coupling terms are not insignificant, and thus the Born-Oppenheimer Approximation cannot be used to assume a diagonal kinetic energy operator. Since a diagonalized kinetic energy operator is necessary for creating solvable differential equations, additional steps must be taken to manipulate the Hamiltonian into a usable form. This new manipulated representation of the Hamiltonian that diagonalizes the kinetic energy operator (but undiagonalizes the potential energy operator) is called the *non-adiabatic* representation, and consequently this branch of quantum chemistry is known as *non-adiabatic* (or *diabatic*) chemistry.

### **The Scattering Matrix**

In non-adiabatic chemistry, diagonalization of the kinetic energy operator leads to a new, undiagonalized potential energy operator and new associated potential energy surfaces. The goal of this thesis is to calculate those potential energy surfaces; however, this is not the complete picture. These surfaces are only a tool with which to construct the *scattering matrix* which describes the dynamics of the system. When constructed, the scattering matrix predicts probabilities of reactions occurring at the molecular level, and thus can be utilized to predict how chemical reactions will proceed. An overview of the construction of the scattering matrix appears in Appendix A.

## Relevance to Air Force

The heavy dependence of the Air Force on chemical studies for materials, fuels, meteorology, etc. makes the study and exploration of non-adiabatic chemistry a necessary step in present and future research. For example, open-shell collisions such as  $\text{N}+\text{O}_2$  or  $\text{O}+\text{N}_2$  that affect the composition of the upper atmosphere may not be adequately described by approximating the derivative coupling terms to zero in the adiabatic representation, and consequently must be studied in the non-adiabatic representation.

The focus of this study is another system of interest, Boron-doped cryogenic hydrogen ( $\text{B}+\text{H}_2$ ), which has an application as a rocket fuel (Yarkony, 1999:i-2). The lowest energy surface (ground state) of the system has a potential well, meaning the system can assume a specific configuration and will not be able to change without outside energy. This well corresponds to the configuration in which the boron atom is close to the center-line of the hydrogen molecule, but does not break the H-H bond. At cryogenic temperatures the system can assume this configuration, storing energy for later extraction when the fuel is burned. This well and the associated stored energy allow  $\text{B}+\text{H}_2$  to be classified as a High Energy Density Material (HEDM).  $\text{B}+\text{H}_2$  also has another low-energy surface, close to but higher than that ground state, which is anti-bonding (meaning there is no potential well). Using the Born-Oppenheimer Approximation to neglect the NAD terms, the adiabatic calculation of these surfaces assumes that the bonding surface and the anti-bonding surface are not associated; that is, that a system in the potential well of the bonding surface will not *couple* to the higher anti-bonding surface. However, if there was significant coupling between the surfaces, the  $\text{B}+\text{H}_2$  molecule could possibly



leave the well and dissociate, shedding its stored energy prematurely, rendering it ineffective as a high energy density fuel. The degree to which this non-coupling assumption is true is not easily extracted from the Hamiltonian in the adiabatic form. Rather, that information lies in the coupling surface—the collection of off-diagonal elements of the non-adiabatic potential energy operator. Hence, in the case of B+H<sub>2</sub>, one must construct the non-adiabatic representation of the Hamiltonian in order to evaluate the probability of coupling, and thus suitability as a high energy density fuel.

### **Recent Work and Problems**

Dr. David R. Yarkony, Johns-Hopkins University, has calculated the adiabatic surfaces for the B+H<sub>2</sub> system as well as the derivative coupling terms through his own software package called *Brooklyn*. *Brooklyn* is a Graphical Unitary Group Approach- (GUGA) based software package that calculates energy levels and molecular wave functions on the Multireference Configuration Interaction (MR-CI) level of theory. At the time of publication *Brooklyn* was not available for public use; an alternative code, *Columbus* developed in Columbus, Ohio originally by I. Shavitt et al. was available for public use, although certain portions of the software suite are still under development (Lischka, undated-a). Since these software packages handle the creation of molecular wave functions and adiabatic energy surfaces, they can be seen as a black box; it is not necessary that the reader understand the underlying theory. Nevertheless, a brief overview of methods to solve the many-body problem is covered in Appendix B.

Since *Brooklyn* and *Columbus* are designed to handle a wide variety of molecules their inputs and outputs for nuclear positions are in terms of Cartesian coordinates. For

most systems including  $B+H_2$  we would prefer to develop a coordinate system that allows for the separation of internal and external dynamics (and thus internal and external Hamiltonians). In the case of the three-body system the internal coordinates are the Jacobi coordinates, where  $r$  gives the bond distance of  $H_2$ ,  $\gamma$  gives the tumbling angle of boron with respect to the hydrogen molecule, and  $R$  gives the distance between boron and the

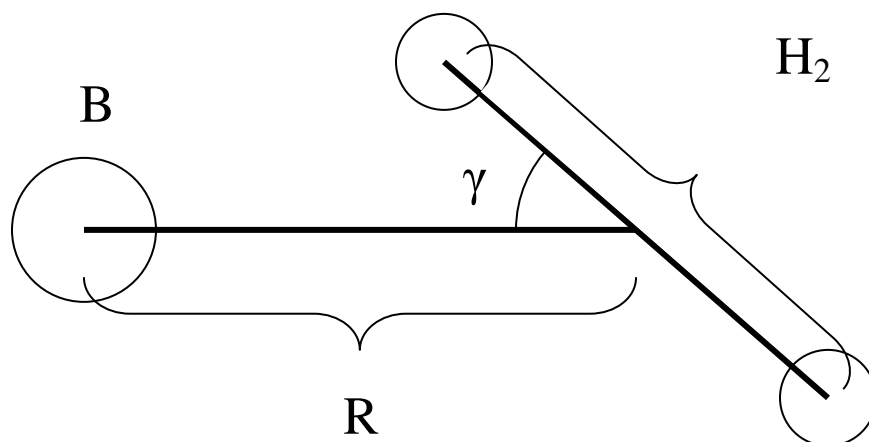


Figure 1. Jacobi Coordinates

center of mass of the hydrogen (see Figure 1). The angle  $\gamma$  can be measured either as the angle shown in Figure 1 or its supplement; for consistency we will always call the lesser of the two angles  $\gamma$ . Because the two hydrogen atoms are indistinguishable it is not necessary to examine the entire cycle of  $\gamma$  from 0 to  $2\pi$ . Throughout the calculations we will only evaluate  $\gamma$  from 0 to  $\pi/2$  because the wave function will be symmetrical in all four quadrants. Another advantage of using Jacobi coordinates is that we can compare the results of these software packages with the work of Dr. Millard Alexander, who calculated some non-adiabatic potential energy surfaces of  $B+H_2$  in Jacobi coordinates for  $r=1.402$ , the equilibrium bond length of the  $H_2$  molecule (Alexander, 1993:6019).

Dr. David Weeks took upon himself the job of transforming Dr. Yarkony's NAD terms from *Brooklyn* into their Jacobi counterparts. These results did not match those of Dr. Alexander. Finding the correction has been the thrust of this thesis, since we cannot construct the proper non-adiabatic potential energy surfaces without knowing the correct NAD terms. To find and correct the error, this study was split into two explorations before being able to confidently construct the non-adiabatic potential energy surfaces: first, determining if the NAD terms produced by *Brooklyn* were correct by attempting to reproduce them with *Columbus*; and second, determining if the method of converting Cartesian NAD terms to their Jacobi counterparts was flawed. The final result is that the *Brooklyn* NAD terms were correct and it was the conversion process that contained the error.

## II. Theory

### The Hamiltonian

As stated in the introduction, the goal of this study is to find the non-adiabatic potential energy surfaces, specifically for B+H<sub>2</sub>. Energy surfaces are no more than a collection of energy eigenvalues each of which is specific to a particular atomic configuration. To find energy eigenvalues we begin at the time independent Schrödinger equation (TISE) (Liboff, 1998:72):

$$(\hat{H} - E) \cdot \Psi = 0. \quad (1)$$

The form expressed in equation (1) is the most basic and abstract way to view the action of the Hamiltonian operator. To be of any use, we must consider it in some coordinate system and apply it to a molecule, at least generally. The Hamiltonian operator for polyatomic molecules in the coordinate representation is written as:

$$\hat{H}_T \equiv -\frac{1}{2} \sum_{\alpha} \frac{1}{M_{\alpha}} \nabla_R^2 - \frac{1}{2} \sum_i \nabla_r^2 - \sum_{i,\alpha} \frac{Z_{\alpha}}{|r_i - R_{\alpha}|} + \sum_{i,j} \frac{1}{|r_i - r_j|} + \sum_{\alpha,\beta} \frac{Z_{\alpha} Z_{\beta}}{|R_{\alpha} - R_{\beta}|} \quad (2)$$

where i and j index electrons,  $\alpha$  and  $\beta$  index the nuclei,  $\mathbf{r}$  is the electronic coordinates and  $\mathbf{R}$  is the nuclear coordinates (Szabo 1996:41). Unless otherwise noted we are using atomic units (au). The terms are:

$-\frac{1}{2} \sum_{\alpha} \frac{1}{M_{\alpha}} \nabla_R^2$	Nuclear Kinetic Energy
$-\frac{1}{2} \sum_i \nabla_r^2$	Electron Kinetic Energy
$-\sum_{i,\alpha} \frac{Z_{\alpha}}{ r_i - R_{\alpha} }$	Nucleus-Electron Interaction
$\sum_{i,j} \frac{1}{ r_i - r_j }$	Electron-Electron Interaction
$\sum_{\alpha,\beta} \frac{Z_{\alpha} Z_{\beta}}{ R_{\alpha} - R_{\beta} }$	Nucleus-Nucleus Interaction.

### The Born-Oppenheimer Approximation

The Born-Oppenheimer approximation assumes that the nuclei move far slower than the electrons (Bransden, 1984:386-88). Thus to the electrons, the nuclei can be seen as standing still, creating a constant (time-independent) potential field. To the nuclei the electrons move so fast that their average can be seen as a constant potential field. For electron dynamics this approximation allows us to assume that the first term of the Hamiltonian (nuclear kinetic energy) is equal to zero, and the last term (potential due to internuclear Coulombic forces) is equal to a constant. The effect of adding a constant to the Hamiltonian is only to add a constant to the eigenvalues; since we can arbitrarily choose the zero of a potential field we can neglect this constant term. The remaining terms form the electronic Hamiltonian:

$$\hat{H}_e \equiv -\frac{1}{2} \sum_i \nabla_r^2 - \sum_{i,\alpha} \frac{Z_{\alpha}}{|r_i - R_{\alpha}|} + \sum_{i,j} \frac{1}{|r_i - r_j|}, \quad (3)$$

which has a complete set of orthogonal electronic eigenfunctions,  $\phi_i(\mathbf{R}; \mathbf{r})$ . Note that, although the nuclear terms are left out of the Hamiltonian, the nuclear configuration is not to be ignored. The functions  $\phi_i(\mathbf{R}; \mathbf{r})$  depend parametrically upon the nuclear coordinates ( $\mathbf{R}$ ) as much as they depend functionally on the electronic coordinates ( $\mathbf{r}$ ). For simplicity I will use abstract notation until necessary to operate in the coordinate representation.

The eigenfunctions,  $\phi_i$ , of the electronic Hamiltonian form a complete and orthogonal set, so that any function, specifically the wave function,  $\psi$ , from equation (1) can be written as a superposition electronic wave functions:

$$|\Psi\rangle = \sum_i F_i |\phi_i\rangle \quad (4)$$

where the value of the  $q^{\text{th}}$  component,  $F_q$ , can be found by:

$$\langle \phi_q | \Psi \rangle = \sum_i F_i \langle \phi_q | \phi_i \rangle = F_i \delta_{i,q} = F_q, \quad (5)$$

where the orthogonality of the electronic states  $\phi_i$  has been used. Since the total Hamiltonian is a product of the nuclear and electronic Hamiltonians (under the Born-Oppenheimer Approximation), the eigenfunctions of the full Hamiltonian can be written as a product of eigenfunctions of those Hamiltonians. Thus if  $|\Psi\rangle$  from equation (4) is an eigenfunction of the total Hamiltonian and  $|\phi_i\rangle$  are the eigenfunctions of the electronic Hamiltonian, it follows that the  $F_i$ 's are the eigenfunctions of the nuclear Hamiltonian, and as such are functions of the nuclear coordinates (this will be key to the approximation shortly).

Since for the electronic Hamiltonian

$$\sum_i \langle \varphi_q | \hat{H}_e | \varphi_i \rangle = \sum_i \langle \varphi_q | E_i | \varphi_i \rangle = E_i \delta_{i,q} = E_q, \quad (6)$$

it follows that for the total Hamiltonian,

$$\hat{H}_T \equiv \hat{H}_e + \hat{H}_N, \quad (7)$$

(where  $\hat{H}_N$  is the nuclear Hamiltonian) we have the following derivation. We start by integrating the TISE in equation (1) with respect to electronic coordinates:

$$\langle \varphi_q | \hat{H}_T | \Psi \rangle = \langle \varphi_q | E | \Psi \rangle. \quad (8)$$

We then substitute for the total Hamiltonian with equation (7) and substitute for  $\psi$  with equation (4),

$$\sum_i \langle \varphi_q | \hat{H}_e + \hat{H}_N | F_i \varphi_i \rangle = \sum_i \langle \varphi_q | E | F_i \varphi_i \rangle \quad (9)$$

which can then be split:

$$\sum_i \langle \varphi_q | \hat{H}_e | F_i \varphi_i \rangle + \sum_i \langle \varphi_q | \hat{H}_N | F_i \varphi_i \rangle = E \sum_i \langle \varphi_q | F_i \varphi_i \rangle. \quad (10)$$

And, taking advantage of (6) we have

$$E_q F_q + \sum_i \langle \varphi_q | \hat{H}_N | F_i \varphi_i \rangle = E F_q \quad (11)$$

or

$$\sum_i \langle \varphi_q | \hat{H}_N | F_i \varphi_i \rangle + (E_q - E) \cdot F_q = 0. \quad (12)$$

We do not yet know how to evaluate the term  $\sum_i \langle \varphi_q | \hat{H}_N | F_i \varphi_i \rangle$ . In order to evaluate it we

must consider it in the coordinate representation. Recall that

$$\hat{H}_N \equiv -\frac{1}{2} \sum_{\alpha} \frac{1}{M_{\alpha}} \nabla_R^2; \quad (13)$$

thus, when operating on the full molecular wave function  $\Psi$ ,

$$\begin{aligned} \langle r | \hat{H}_N | \Psi \rangle &= \hat{H}_N \sum_i F_i(R) \cdot \varphi(R; r) = \\ &= \frac{1}{2} \sum_{\alpha, i} \frac{1}{M_{\alpha}} \left\{ \left( \nabla_R^2 F_i(R) \right) \cdot \varphi_i(R; r) + 2 \left( \bar{\nabla}_R F_i(R) \right) \cdot \left( \bar{\nabla}_R \varphi_i(R; r) \right) + F_i(R) \cdot \left( \nabla_R^2 \varphi_i(R; r) \right) \right\} \end{aligned} \quad (14)$$

where we have merely used the product rule for derivatives. Notice the pair of terms  $\left( \nabla_R^2 F_i(R) \right) \cdot \varphi_i(R; r)$  and  $\left( \bar{\nabla}_R \varphi_i(R; r) \right)$ . These terms take derivatives of the electronic wave functions with respect to nuclear coordinates. These terms, when integrated with respect to electronic coordinates become the derivative coupling terms set forth in the introduction. The Born-Oppenheimer Approximation allows us to assume that derivatives of the electronic wave function with respect to the nuclear coordinates are negligible; that is,  $\nabla_{\alpha} \varphi_q$  and  $\nabla_{\alpha}^2 \varphi_q$  are zero, so

$$\langle r | \hat{H}_N | \Psi \rangle = \hat{H}_N \sum_i F_i(R) \cdot \varphi(R; r) = \frac{1}{2} \sum_{\alpha, i} \frac{1}{M_{\alpha}} \left\{ \left( \nabla_R^2 F_i(R) \right) \cdot \varphi_i(R; r) \right\}. \quad (15)$$

This leads to another uncoupled TISE. If we now substitute the result of (15) into (12)

we get:

$$\frac{1}{2} \sum_{\alpha} \frac{1}{M_{\alpha}} \nabla_R^2 F_q + (E_q - E) \cdot F_q = 0 \quad (16)$$

or, rearranging the terms into an eigenvalue equation,

$$\left( \frac{1}{2} \sum_{\alpha} \frac{1}{M_{\alpha}} \nabla_R^2 + E_q \right) \cdot F_q(R) = E F_q(R). \quad (17)$$



Equation (17) is the nuclear TISE, with  $F_q(\mathbf{R})$  as its eigenfunctions.  $E_q(\mathbf{R})$ , the eigenvalues for the electronic wave equation, now become the effective potential for the nuclear wave equation. The Hamiltonian is broken into two operators, kinetic and potential energy, which can be represented as matrices operating on the nuclear wave function. Since the TISE is an eigenvalue equation, we can refer to the nuclear wave functions as its eigenvectors or eigenfunctions.

Using the Born-Oppenheimer approximation, forming matrix operators out of the Hamiltonian is simple. Before we do, however, we must discuss truncation of the energy surfaces.

### **Basis and Symmetry**

For the B+H<sub>2</sub> system, there are an infinite number of molecular orbitals, each of which has an associated energy surface, that could be taken into account (Szabo, 1996:55-57). These molecular orbitals serve as basis vectors for forming the nuclear wave functions. It is of course impossible to build the infinite matrix associated with such a basis. Even a small number of these surfaces will begin to present numerical difficulties (Szabo, 1996:58). In order to keep calculations to a minimum but still arrive at worthwhile results, we will only consider the molecule in its electronic ground state. At the very low temperatures at which this system is of interest as a cryogenic fuel, these are the only energy levels of interest.

A peculiarity of this molecule is that the valence electron of boron has three choices of atomic orbital for its ground state owing to the three-fold degeneracy of the p-orbital (Alexander, 1996:6015). At the asymptotic limit, when boron is very far from

hydrogen, the eigenvalues of these three choices of orbital are degenerate; but as  $\text{H}_2$  and B come together the energy surfaces associated with these three ground states begin to separate, but are still closer together than higher states. For this reason we will only consider the three energy surfaces that arise from the system's occupying each of three molecular orbitals, each of which is composed primarily of only one of boron's atomic p-orbitals for our energy levels of interest. Thus all the nuclear wave functions we consider will be linear combinations of these three molecular orbitals.

Special note should be taken that since  $\text{B}+\text{H}_2$  has only three atoms, it can always be placed in a plane. Thus, except for the linear and perpendicular configurations, the system has the highest symmetry of  $C_s$ , meaning the only non-identity symmetry it has is reflection through the plane of the molecule (Bishop, 1993:37). The molecular orbitals can thus be symmetric across the plane, which are given a symmetry label  $A'$  or antisymmetric, which are given a symmetry label  $A''$ . Figure 2 shows an example of symmetric and antisymmetric orbitals with respect to the x-y plane. As it turns out the three ground states for the system include one wave function of  $A''$  symmetry labeled

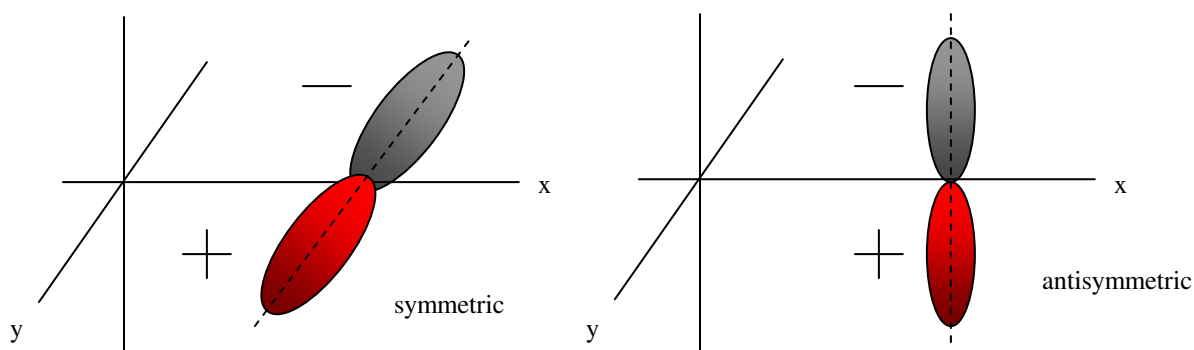


Figure 2. Symmetric vs. antisymmetric p-orbitals when reflected through the x-y plane

1A'', and two of A' symmetry labeled 1A' and 2A' (Alexander, 1993:6018). Each molecular orbital has an associated potential energy surface which carries the same label.

If we consider three possible molecular orbitals then equation (17) in matrix form becomes:

$$\left\{ \begin{bmatrix} \frac{1}{2} \sum_{\alpha} \frac{1}{M_{\alpha}} \nabla_R^2 & 0 & 0 \\ 0 & \frac{1}{2} \sum_{\alpha} \frac{1}{M_{\alpha}} \nabla_R^2 & 0 \\ 0 & 0 & \frac{1}{2} \sum_{\alpha} \frac{1}{M_{\alpha}} \nabla_R^2 \end{bmatrix} + \begin{bmatrix} 1A' & 0 & 0 \\ 0 & 2A' & 0 \\ 0 & 0 & 1A'' \end{bmatrix} \right\} \begin{bmatrix} F_1 \\ F_2 \\ F_3 \end{bmatrix} = E \begin{bmatrix} F_1 \\ F_2 \\ F_3 \end{bmatrix} \quad (18)$$

(Weeks, 2004).

Note that the number of molecular orbitals we wish to consider determines the dimensions of the operator matrix. Hence we can think of doing algebra in a three-space, where the three molecular orbitals serve as basis vectors. Since the potential matrix has no off-diagonal elements, this is the *adiabatic* representation. This condition assures that a nuclear wave function on one potential energy surface does not interfere with the function on another. Since the Born-Oppenheimer Approximation allows that the off-diagonal elements of the kinetic energy operator be assumed negligible, it is diagonal as well and we can extract solvable equations from this eigenvalue equation where nuclear dynamics on each of the 1A', 2A', and 1A'' surfaces is uncoupled.

### Refining the Approximation

We will now consider the situations in which the Born-Oppenheimer Approximation cannot be used to go from equation (14) to equation (15). That is, the derivatives of the electronic wave functions with respect to the nuclear positions or NAD

terms are significantly greater than zero, and must be included. Recall that these terms are the off-diagonal terms of the kinetic energy matrix in equation (18). When these terms are included, the potential energy matrix remains diagonalized, but the kinetic energy matrix is not. The result, from equation (14), is

$$\begin{aligned}
 & \left\{ \begin{bmatrix} \frac{1}{2} \sum_{\alpha} \frac{1}{M_{\alpha}} \nabla_R^2 & 0 & 0 \\ 0 & \frac{1}{2} \sum_{\alpha} \frac{1}{M_{\alpha}} \nabla_R^2 & 0 \\ 0 & 0 & \frac{1}{2} \sum_{\alpha} \frac{1}{M_{\alpha}} \nabla_R^2 \end{bmatrix} + \right. \\
 & \left. \begin{bmatrix} \sum_{\alpha} \frac{1}{M_{\alpha}} \int dr \varphi_1^* [\bar{\nabla}_R \varphi_1 \cdot \bar{\nabla}_R + \nabla_R^2 \varphi_1] & \sum_{\alpha} \frac{1}{M_{\alpha}} \int dr \varphi_1^* [\bar{\nabla}_R \varphi_2 \cdot \bar{\nabla}_R + \nabla_R^2 \varphi_2] & \sum_{\alpha} \frac{1}{M_{\alpha}} \int dr \varphi_1^* [\bar{\nabla}_R \varphi_3 \cdot \bar{\nabla}_R + \nabla_R^2 \varphi_3] \\ \sum_{\alpha} \frac{1}{M_{\alpha}} \int dr \varphi_2^* [\bar{\nabla}_R \varphi_1 \cdot \bar{\nabla}_R + \nabla_R^2 \varphi_1] & \sum_{\alpha} \frac{1}{M_{\alpha}} \int dr \varphi_2^* [\bar{\nabla}_R \varphi_2 \cdot \bar{\nabla}_R + \nabla_R^2 \varphi_2] & \sum_{\alpha} \frac{1}{M_{\alpha}} \int dr \varphi_2^* [\bar{\nabla}_R \varphi_3 \cdot \bar{\nabla}_R + \nabla_R^2 \varphi_3] \\ \sum_{\alpha} \frac{1}{M_{\alpha}} \int dr \varphi_3^* [\bar{\nabla}_R \varphi_1 \cdot \bar{\nabla}_R + \nabla_R^2 \varphi_1] & \sum_{\alpha} \frac{1}{M_{\alpha}} \int dr \varphi_3^* [\bar{\nabla}_R \varphi_2 \cdot \bar{\nabla}_R + \nabla_R^2 \varphi_2] & \sum_{\alpha} \frac{1}{M_{\alpha}} \int dr \varphi_3^* [\bar{\nabla}_R \varphi_3 \cdot \bar{\nabla}_R + \nabla_R^2 \varphi_3] \end{bmatrix} + \right. \\
 & \left. \begin{bmatrix} E_1 & 0 & 0 \\ 0 & E_2 & 0 \\ 0 & 0 & E_3 \end{bmatrix} \right) \begin{bmatrix} F_1 \\ F_2 \\ F_3 \end{bmatrix} = E \begin{bmatrix} F_1 \\ F_2 \\ F_3 \end{bmatrix}
 \end{aligned}
 \tag{19}$$

Upon inspection it can be seen that this is the same as equation (18), but to the kinetic energy operator has been added a 3x3 matrix of derivative coupling operators. To further simplify this representation, we recognize that

$$P_{ij}(R) \equiv \int dr \varphi_i^*(R; r) \cdot \bar{\nabla}_R \varphi_j(R; r) \tag{20}$$

is just a constant dotted into the del operator and

$$Q_{ij}(R) \equiv \int dr \varphi_i^*(R; r) \cdot \nabla_R^2 \varphi_j(R; r) \tag{21}$$

is also a constant. Note that the differential operator is with respect to nuclear coordinates but the integral is with respect to electronic coordinates. These are the derivative coupling terms. Hence we can write the Hamiltonian as

$$\begin{aligned}
 & \left\{ \begin{bmatrix} \frac{1}{2} \sum_{\alpha} \frac{1}{M_{\alpha}} \nabla_R^2 & 0 & 0 \\ 0 & \frac{1}{2} \sum_{\alpha} \frac{1}{M_{\alpha}} \nabla_R^2 & 0 \\ 0 & 0 & \frac{1}{2} \sum_{\alpha} \frac{1}{M_{\alpha}} \nabla_R^2 \end{bmatrix} + \right. \\
 & \left. \begin{bmatrix} \sum_{\alpha} \frac{1}{M_{\alpha}} [P_{11} \cdot \bar{\nabla}_R + Q_{11}] & \sum_{\alpha} \frac{1}{M_{\alpha}} [P_{12} \cdot \bar{\nabla}_R + Q_{12}] & 0 \\ \sum_{\alpha} \frac{1}{M_{\alpha}} [P_{21} \cdot \bar{\nabla}_R + Q_{21}] & \sum_{\alpha} \frac{1}{M_{\alpha}} [P_{22} \cdot \bar{\nabla}_R + Q_{22}] & 0 \\ 0 & 0 & \sum_{\alpha} \frac{1}{M_{\alpha}} [P_{33} \cdot \bar{\nabla}_R + Q_{33}] \end{bmatrix} + \right. \quad (22) \\
 & \left. \begin{bmatrix} E_1 & 0 & 0 \\ 0 & E_2 & 0 \\ 0 & 0 & E_3 \end{bmatrix} \right\} \begin{bmatrix} F_1 \\ F_2 \\ F_3 \end{bmatrix} = E \begin{bmatrix} F_1 \\ F_2 \\ F_3 \end{bmatrix}
 \end{aligned}$$

Ordinarily the 13, 23, 31, and 32 elements of the second matrix would be non-zero as well; however, the 1A' and 2A' molecular orbitals, which are primarily composed of the atomic p-orbitals of boron that are coplanar with the system tend to mix with each other, but not with the 1A'' molecular orbital, which is composed primarily of the atomic p-orbital orthogonal to the plane. Thus we save CPU time by recognizing that those elements, which represent mixing of the third with either of the first two, are nearly zero (Alexander, 1993:6019).

### The Diabatic Transformation

If we were satisfied with the adiabatic representation we could stop here; unfortunately without employing the Born-Oppenheimer Approximation this

representation does not provide a set of differential equations which are solvable. If, however, the kinetic energy matrices are considered in a different basis in which they are diagonalized we will form three new *adiabatic* potential energy surfaces and a set of *adiabatic* equations that are tractable.

In order to understand how to diagonalize the kinetic energy operator, consider that the three molecular orbitals  $1A'$ ,  $1A''$ , and  $2A'$  are the basis vectors of a wave function three-space. Consider a nuclear wave function,  $F$ , to be a vector in this three-space, as depicted in Figure 3. One could imagine splitting this vector into three components, one along each of the axes. This depiction corresponds to constructing the wave function from a linear combination of these molecular orbitals, or finding parts of

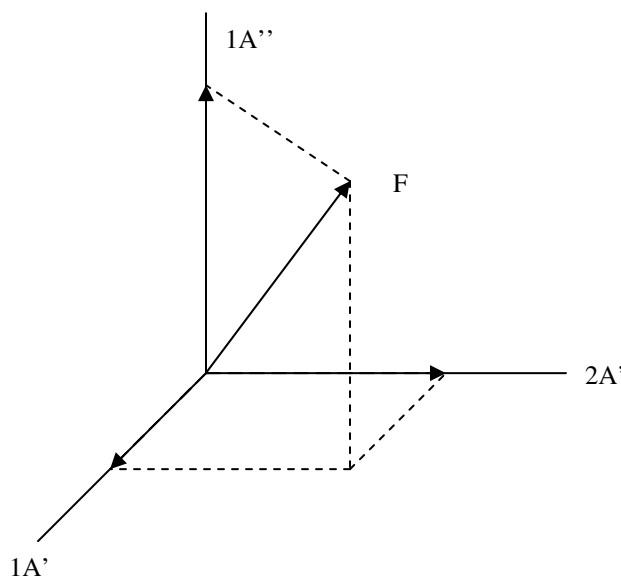


Figure 3. A Nuclear Wave Vector Represented in Wave Function Three-Space

the total wave function on all three potential energy surfaces. A linear operator,  $\hat{O}$ , that acts on  $F$  will act on the components of  $F$  individually, as one might expect simple in

linear algebra. If  $\hat{O}$  is diagonal, then the result of  $\hat{O}(F_i)$  is also along component  $i$  (where  $i$  is  $1A'$ ,  $1A''$ , or  $2A'$ ). If  $\hat{O}$  is not diagonal, but there exist three eigenvectors of  $\hat{O}$  which form an alternative basis for the three-space, then  $\hat{O}$  is diagonalizable in that basis (Hoffman, 1971:185). The diagonalization takes the form of pre- and post-multiplication by a rotation operator,  $T$  (created with knowledge of the inner products of the original basis vectors and the eigenvectors of  $\hat{O}$ ) such that

$$\hat{O}_D = T\hat{O}T^{-1} \quad (23)$$

where  $\hat{O}_D$  is the representation of  $\hat{O}$  in the new basis, and is diagonal. The basis vectors of this new basis are the eigenvectors of  $\hat{O}$  used to create the rotation operator. They will be some mixture of the original basis vectors, as illustrated in Figure 4. This mixing

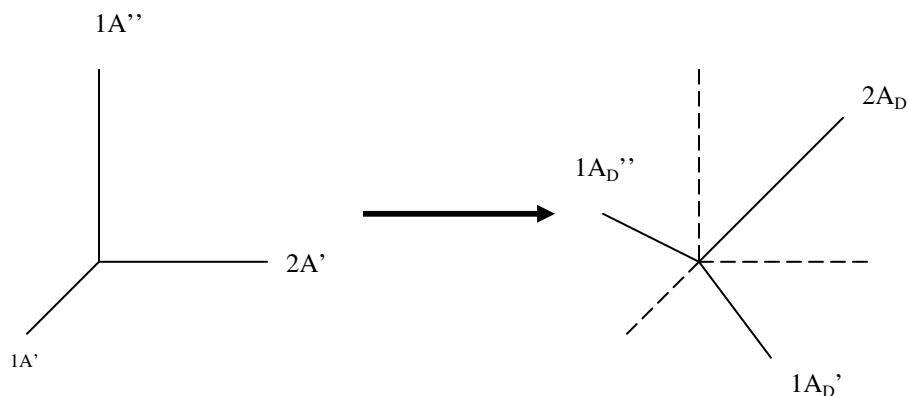


Figure 4. Rotation of Potential Energy Surface Basis

depicts the change from molecular orbitals and potential energy surfaces in the adiabatic representation to molecular orbitals and potential energy surfaces in the non-adiabatic representation. The  $1A'$ ,  $2A'$  and  $1A''$  vectors are eigenfunctions of the adiabatic

potential energy operator, and the  $1A_D'$ ,  $2A_D'$  and  $1A_D''$  vectors are the eigenfunctions of the diabatic kinetic energy operator.

From equation (22) we know that our kinetic energy operator which we shall call  $K$  is not diagonal. Creating the rotation operator matrix to diagonalize  $K$  would normally require three angles of rotation that mix the old molecular orbitals into new ones. But since the  $1A''$  orbital does not mix with the others, we need only worry about mixing the two  $A'$  orbitals which requires only a single angle  $\Theta(\mathbf{R})$  (Koppel 2002:7). This rotation, applied the matrix-form Hamiltonian, will reduce the  $P(\mathbf{R})$  and  $Q(\mathbf{R})$  terms to zero. The rotation matrix takes the form

$$T \equiv \begin{bmatrix} \cos(\Theta(R)) & \sin(\Theta(R)) & 0 \\ -\sin(\Theta(R)) & \cos(\Theta(R)) & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad (24)$$

such that

$$K' \equiv TKT^{-1}; U' \equiv TUT^{-1} \quad (25)$$

where  $U$  is the potential energy operator and the primed matrices are the kinetic and potential energy operators in the diabatic representation. In this representation,

$$K' = \begin{bmatrix} \frac{1}{2} \sum_{\alpha} \frac{1}{M_{\alpha}} \nabla_R^2 & 0 & 0 \\ 0 & \frac{1}{2} \sum_{\alpha} \frac{1}{M_{\alpha}} \nabla_R^2 & 0 \\ 0 & 0 & \frac{1}{2} \sum_{\alpha} \frac{1}{M_{\alpha}} \nabla_R^2 \end{bmatrix} \quad (26)$$

and



$$U' = \begin{bmatrix} E'_{11} & E'_{12} & 0 \\ E'_{12} & E'_{22} & 0 \\ 0 & 0 & E'_{33} \end{bmatrix}. \quad (27)$$

$E'_{11}$ ,  $E'_{22}$ , and  $E'_{33}$  are the diabatic (or non-adiabatic) potential energy surfaces upon which we can propagate the wave functions; and  $E'_{12}$ , though not a proper potential surface, is the coupling value between the first two surfaces.  $[K'+U']\mathbf{F}=\mathbf{EF}$  is now a solvable system of equations, and furthermore we have a measure of coupling between the potential energy surfaces.

The task now turns to identifying  $\Theta(\mathbf{R})$ , which will depend on  $\mathbf{P}(\mathbf{R})$  and  $\mathbf{Q}(\mathbf{R})$ . As an approximation, let us assume that  $\mathbf{Q}(\mathbf{R})$ , which is a double derivative of electronic eigenfunctions with respect to nuclear coordinates, is negligible compared to  $\mathbf{P}(\mathbf{R})$  which is only a single derivative of the same. Recall from equation (20) that  $P_{ij}$  has the form

$$P_{ij}(R) \equiv \int dr \varphi_i^*(R;r) \cdot \bar{\nabla}_R \varphi_j(R;r) \quad (20)$$

or, abstractly,

$$P_{ij} \equiv \langle \varphi_i | \bar{\nabla}_R \varphi_j \rangle. \quad (28)$$

In what Horst Koppel calls the “off-diagonal analogue of the Hellmann-Feynman theorem” we can manipulate the NAD term into a more useable formula (2002:5). Let us start again with the TISE:

$$\hat{H}|\varphi_j\rangle = E_j|\varphi_j\rangle. \quad (29)$$

We then take the gradient with respect to the nuclear coordinates:

$$\bar{\nabla}(\hat{H}|\varphi_j\rangle) = \bar{\nabla}(E_j|\varphi_j\rangle) \quad (30)$$

which by the product rule becomes

$$\bar{\nabla} \hat{H} |\varphi_j\rangle + \hat{H} |\bar{\nabla} \varphi_j\rangle = \bar{\nabla} E_j |\varphi_j\rangle + E_j |\bar{\nabla} \varphi_j\rangle. \quad (31)$$

Now integrate this equation over electronic coordinates:

$$\langle \varphi_i | \bar{\nabla} \hat{H} | \varphi_j \rangle + \langle \varphi_i | \hat{H} | \bar{\nabla} \varphi_j \rangle = \langle \varphi_i | \bar{\nabla} E_j | \varphi_j \rangle + \langle \varphi_i | E_j | \bar{\nabla} \varphi_j \rangle. \quad (32)$$

Both energy terms on the right-hand side of the equation are constants and can be removed from the integration, while the Hamiltonian in the second term on the left-hand side of equation (32) can act on the bra rather than the ket:

$$\langle \varphi_i | \bar{\nabla} \hat{H} | \varphi_j \rangle + E_i \langle \varphi_i | \bar{\nabla} \varphi_j \rangle = \bar{\nabla} E_j \langle \varphi_i | \varphi_j \rangle + E_j \langle \varphi_i | \bar{\nabla} \varphi_j \rangle. \quad (33)$$

We now have an equation which has the NAD term in it. Elimination of the first term on the right-hand side by orthogonality and simple algebraic manipulation reveal a new formula for the NAD term:

$$P_{ij} \equiv \langle \varphi_i | \bar{\nabla} \varphi_j \rangle = \frac{\langle \varphi_i | \bar{\nabla} \hat{H} | \varphi_j \rangle}{E_j - E_i}. \quad (34)$$

For an overview of how *Columbus* calculates  $P_{ij}$ , see Appendix C. This form of the derivative coupling term brings to light one situation where the Born-Oppenheimer approximation cannot be applied to the adiabatic representation. In the denominator of the term is the difference between the two energy surfaces  $i$  and  $j$ . As they become close, the derivative coupling term becomes large and cannot be neglected. Moreover, at the point where the surfaces cross the term becomes a singularity, creating havoc with adiabatic predictions.

Advantage may be taken upon examining the symmetry of the electronic wave functions in the NAD term. Since  $\bar{\nabla}$  is a symmetric operator, if one of the wave functions

integrated in  $P_{ij}$  is symmetric but the other is antisymmetric, the entire integral is antisymmetric over all space, and is zero. This is why no coupling is possible (at this level of theory) between the  $A'$  and  $A''$  states, and thus why when we consider the derivative coupling terms, we shall only consider the terms that couple  $1A'$  and  $2A'$ .

The new  $P'_{ij}$  of the diabatic representation will be related to the adiabatic  $P_{ij}$  by a gauge transformation (Koppel, 2002:7):

$$P'_{ij}(R) = P_{ij}(R) + \bar{\nabla}(\Theta(R)). \quad (35)$$

We want to set this to zero, so

$$\bar{\nabla}(\Theta(R)) = -P_{ij}(R) = P_{ji}(R). \quad (36)$$

Solving for  $\Theta(\mathbf{R})$  simply requires integration of this equation:

$$\Theta(R) = -\int_0^R dR' \cdot P_{ij}(R') + \Theta(R_0), \quad (37)$$

where  $\Theta(\mathbf{R}_0)$  represents an arbitrary point at which to begin the line integral.

### III. Calculation, Results and Discussion

#### *Columbus and Brooklyn*

The software suite of choice for this venture was *Columbus*. Though operation required a delicate touch, input scripts were cryptic, and documentation was scarce, in the end *Columbus* was the only package available to the public that could compute derivative coupling terms necessary for a diabatic transformation. When computing energy eigenvalues and derivative coupling terms, *Columbus* implements multireference configuration-interaction (MR-CI) (Lischka, 2004). In addition to *Columbus*, it should be noted that we also used results from *Brooklyn*, proprietary code of Dr. Yarkony. Since Dr. Yarkony has aided in writing *Columbus* it is safe to assume that the functions that the two packages have in common are very similar.

*Columbus* itself is not a single program, but a suite of different programs communicating via files. This modular nature allows the user to utilize some parts of *Columbus* without having to bother with others. In order to get derivative coupling terms as we needed, *Columbus* must summon up a dozen or more individual programs to create bases, construct molecular wave functions, make distinct row tables, etc. Each one of these programs individually requires a number of input files which are not easily constructed by hand. For this reason the maintainers of *Columbus* have created a script file *COLINP.X* which guides the user through choices of input and intended output and creates the necessary files. Like the rest of *Columbus*, *COLINP.X* is a work in progress and still requires some manual tweaking of the files after they are created. It also creates a file input for *RUNC.X*, another script file that will call the necessary programs within

*Columbus* that are needed so the user does not have to load each program individually.

More information about the operation and capabilities of *Columbus* can be found at the *Columbus* web site (Lischka, undated-b).

## Coordinates

Because *Columbus* and *Brooklyn* work in Cartesian coordinates it was necessary to convert our Jacobi coordinates into Cartesians for entry into the software packages. Since each of the three atoms must have its position fixed in space, we must translate three Jacobi coordinates into nine Cartesian coordinates. Obviously the molecule can be restricted to the  $z=0$  plane, eliminating the need for three extraneous coordinates. Within the  $x$ - $y$  plane the three Jacobi coordinates specify how the atoms are oriented with respect to one another, but there is still no criterion for how the molecule should be oriented

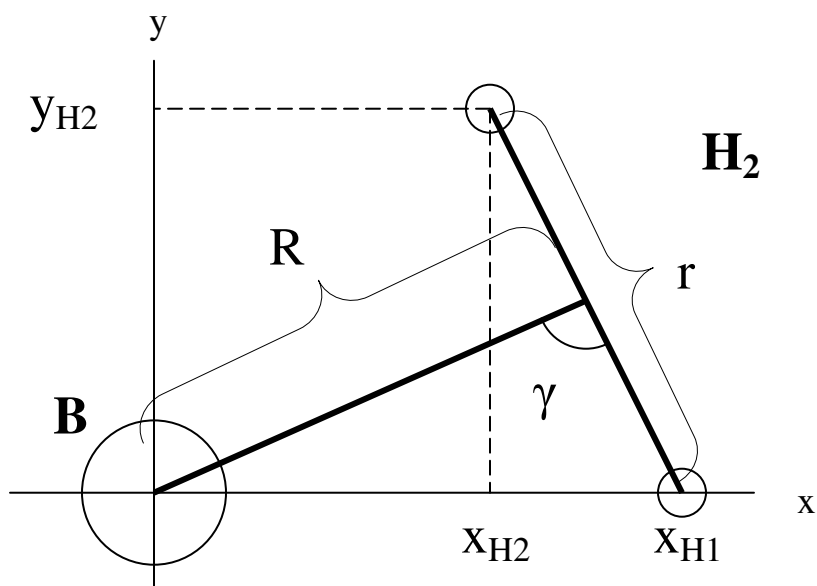


Figure 5. Translating Jacobi Coordinates into Cartesian Coordinates

within that plane. At the request of Dr. Yarkony, a decision was made so that the least number of Cartesian coordinates, three, were needed to specify the geometry (Weeks, 2004). This necessitated the pinning of boron to the origin, pinning one hydrogen to the x-axis but allowing it to slide along it, and allowing the second hydrogen atom to be oriented freely in the plane (see Figure 5). This restriction allowed the geometry to be specified with three Cartesian coordinates:  $x_{H1}$ ,  $x_{H2}$ , and  $y_{H2}$ . Given Jacobi coordinates  $r$ ,  $R$ , and  $\gamma$ , the Cartesian coordinates can be calculated by

$$x_{H1} = \sqrt{R^2 + \frac{r^2}{4} - Rr \cos(\gamma)}, \quad (38)$$

$$y_{H2} = \frac{Rr \sin(\gamma)}{x_{H1}}, \quad (39)$$

and

$$x_{H2} = x_{H1} \pm \sqrt{r^2 - y_{H2}^2} \quad (40)$$

where the sign in equation (40) is equal to the sign of the dot product of the vector along  $r$  and the x axis.

### Calculating the Adiabatic Potential Energy Surfaces

There are three surfaces of interest corresponding to the three molecular orbitals  $1A'$ ,  $2A'$  and  $1A''$  as mentioned previously. A slice of these three surfaces as calculated by *Columbus* is shown in Figure 6. Notice that as  $R$  goes to infinity, that is as the boron atom and the hydrogen molecule become separated, the three energy surfaces tend to become degenerate. The left side of the graph shows the large potential energy barrier to becoming  $BH_2$ . Figure 7 shows an expanded view of the flat region of the surfaces.

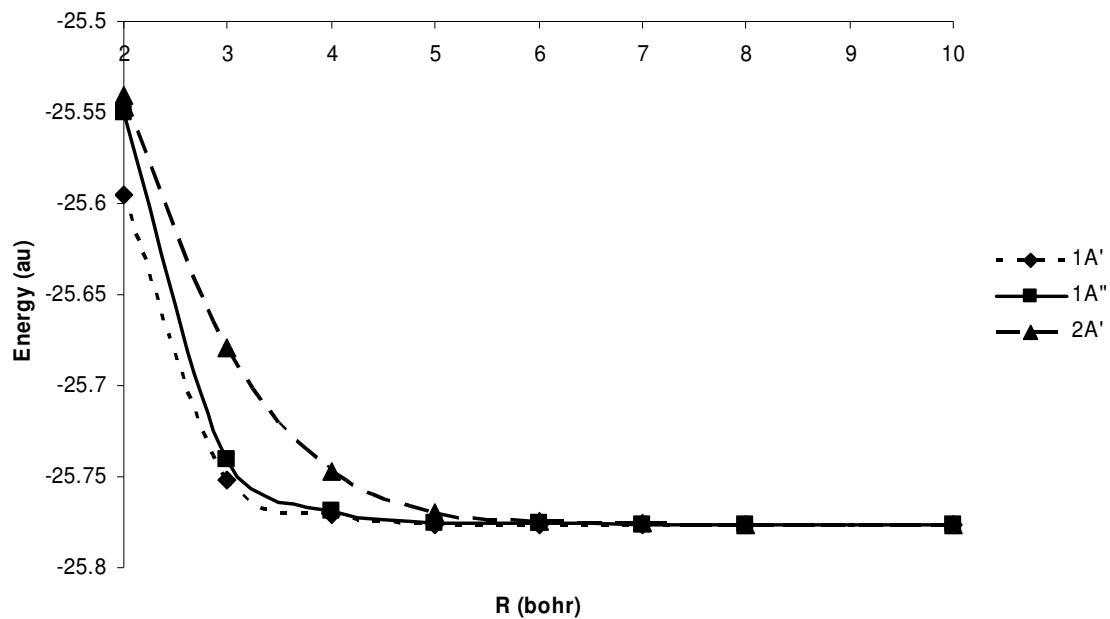


Figure 6. Energy Surface Slice for  $r=1.402$ ,  $\gamma=\pi/4$

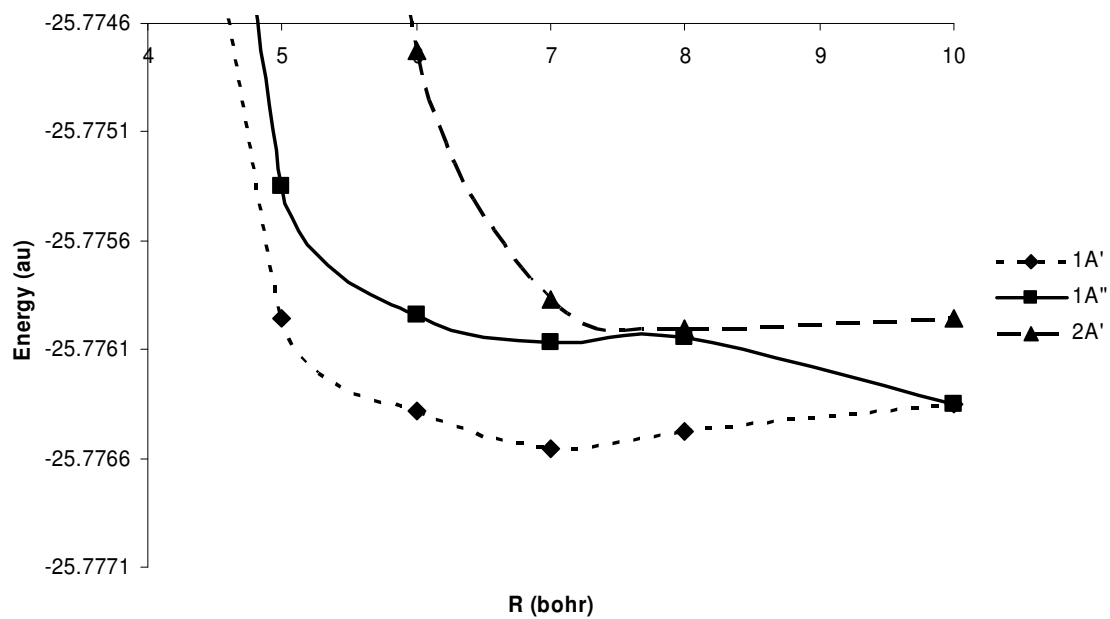


Figure 7. Bonding vs. Anti-bonding States

Notice that the  $1A'$  state does indeed have a small well for bonding, whereas the  $2A'$  state is anti-bonding.  $1A''$  is also bonding, but cannot be coupled to the others because of symmetry. Both of these graphs show the slice of the energy surface taken at  $\gamma = \pi/4$ . The deepest part of the well actually occurs at  $\gamma = \pi/2$ .

Let us also look at the surface as sliced through  $\gamma$ . Figure 8, Figure 9, and Figure 10 all show slices of the energy surfaces at  $R=5.0$  and  $r=1.402$  bohr (equilibrium distance for hydrogen molecule) but calculated in different manners. Figure 8 and Figure 9 both show the same slice of the energy surfaces as calculated by *Columbus*, but there is a difference in input. *Columbus* builds molecular orbitals out of a linear combination of atomic orbitals. In theory there are an infinite number of atomic orbitals available, but in practice we must choose a finite number to serve as a basis set for constructing the

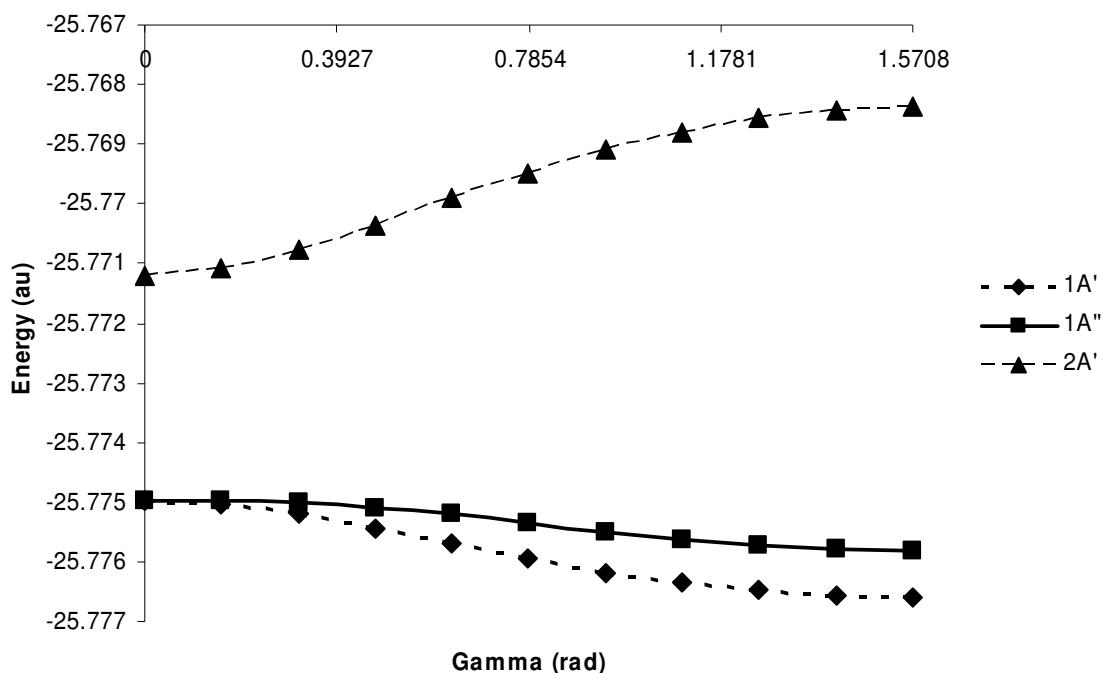


Figure 8. Energy Surface Slice for  $R=5.0$   $r=1.402$



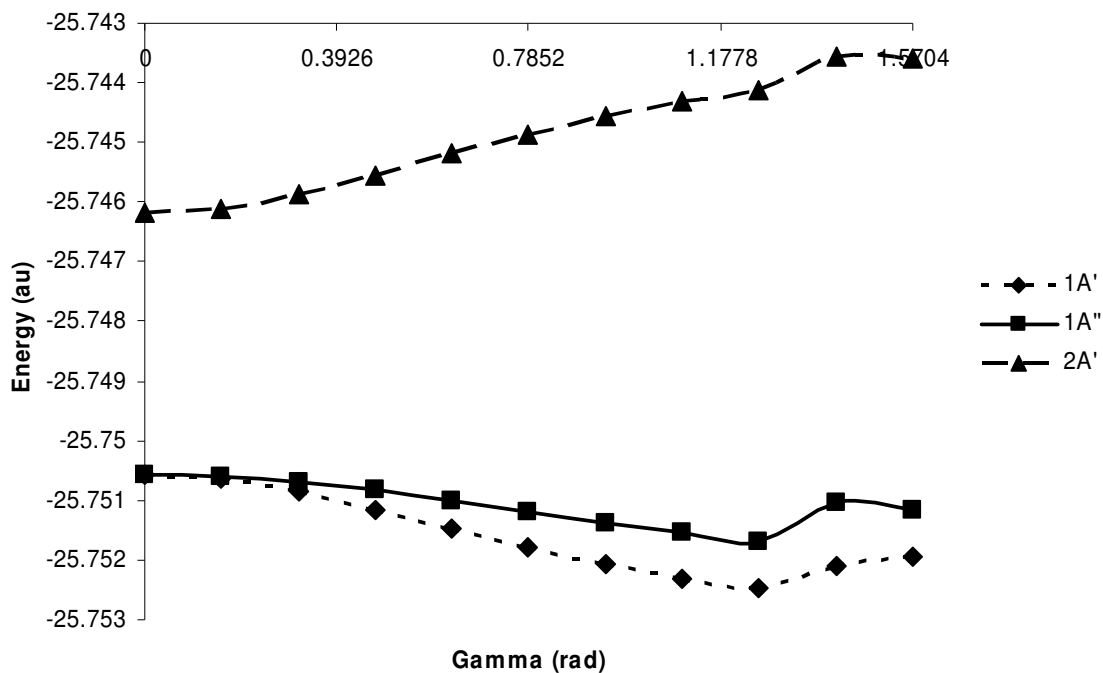


Figure 9. Energy Surface Slice for  $R=5.0$   $r=1.402$ , Truncated Basis

molecular orbitals (this is not to be confused with the basis of molecular orbitals which form a basis of the wave function three-space). Figure 8 shows the potential energy surfaces as calculated with the triple zeta (PVTZ) basis set; in the case of  $B+H_2$  this set consists of 58 basis orbitals, 40 of  $A'$  symmetry and 18 of  $A''$  symmetry. Figure 9 shows the same potential energy surface slice as calculated with the double zeta (PVDZ) basis set; in the case of  $B+H_2$  this set consists of 24 basis orbitals, 18 of  $A'$  symmetry and 6 of  $A''$  symmetry. Notable differences include a difference in energy level and a kink in the PVDZ energy curves. The PVTZ energy surfaces start below the PVDZ set by at about 0.02 atomic units. The variation principle states that the energy calculated using the true Hamiltonian is always an upper bound to the true energy, suggesting that the triple zeta calculations are more accurate. Figure 10 shows data collected from Dr. Yarkony's

calculations using

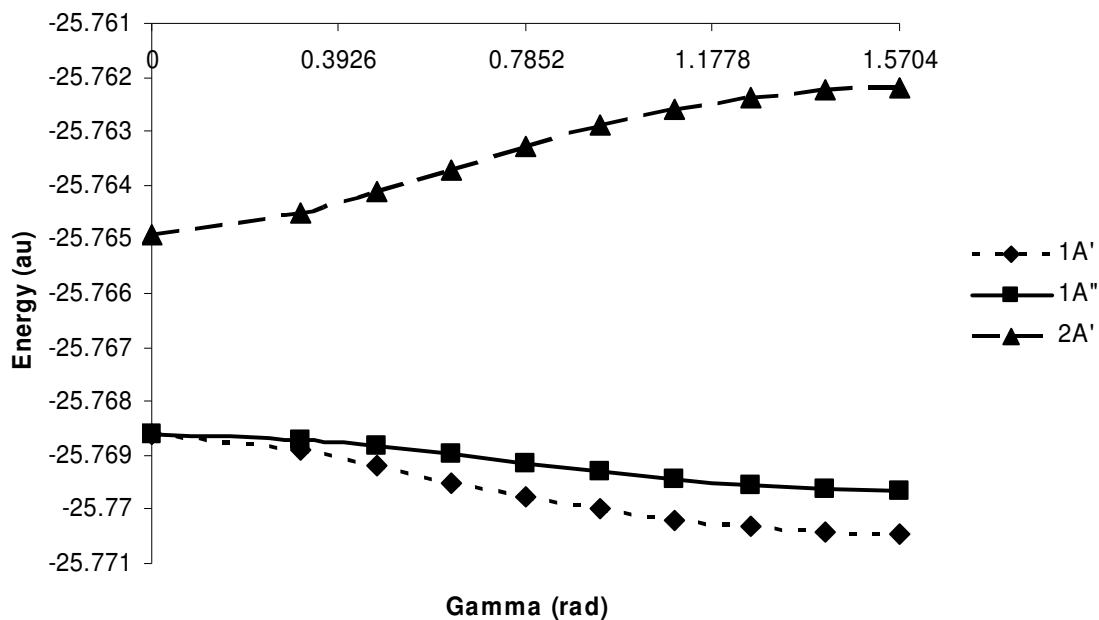


Figure 10. Energy Surface Slice for  $R=5.0$   $r=1.402$ , Brooklyn Code

*Brooklyn*. As best we can tell by examining his input files he is using 83 atomic orbitals in his basis set. This could suggest mixing PVTZ and PVDZ bases or some other basis set. Despite the larger basis set, Dr. Yarkony's energy surfaces seem to come short of *Columbus*' PVTZ calculations by about 0.005 atomic units. Although either of these calculations could be considered sufficient, it may suggest that the method *Columbus* uses to calculate adiabatic energy surfaces is more efficient or more in-depth than that of *Brooklyn*. Figure 11 shows surface and contour plots of the three adiabatic potential energy surfaces of interest as calculated with *Brooklyn* for the equilibrium position of hydrogen,  $r=1.402$ , for the range  $R=5$  to 10 and  $\gamma=0$  to  $\pi$ .

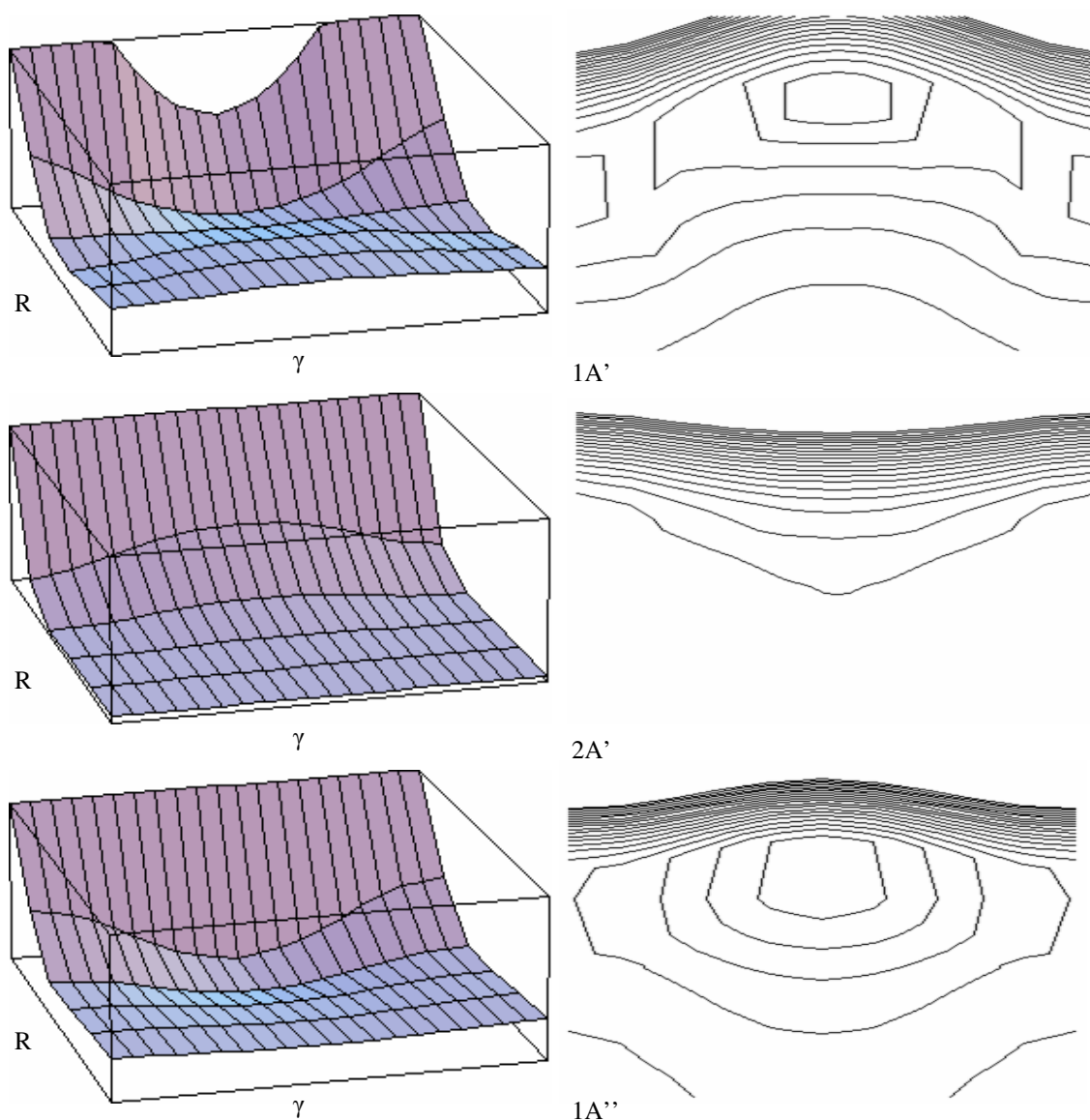


Figure 11. Surface and Contour Plots of the 1A', 2A', and 1A'' Surfaces

### Calculating the Derivative Coupling Terms

Another function of *Columbus* or *Brooklyn* which is critical to calculating the non-adiabatic potential energy surfaces is calculation of the derivative coupling terms. When either program calculates wave functions, it only does so to within a phase factor (Weeks, 2004). When the electronic wave functions are integrated to get the NAD terms,

this phase factor is integrated out for diagonal terms:

$$P_{ii} = \langle \varphi_i e^{i\theta_i} | \bar{\nabla} \varphi_i e^{i\theta_i} \rangle = e^{-i\theta_i} e^{i\theta_i} \langle \varphi_i | \bar{\nabla} \varphi_i \rangle = \langle \varphi_i | \bar{\nabla} \varphi_i \rangle. \quad (41)$$

But for off-diagonal terms where  $\theta_i$  does not equal  $\theta_j$  the phase factor does not disappear. Fortunately for real wave functions the phase factor is always real, so the phase factor just becomes an arbitrary 1 or -1 in front of every calculated NAD term. Unfortunately there is no easy fix to this phase factor, but neither can it be ignored. The only way to correct for it is to view the NAD terms in sequence across the energy surface and invert terms that seem out of place. The two guiding facts for selecting those terms in need of inversion are that the NAD terms should vary slowly across all parts of the surface and that the phase factor is the same for all NAD terms at a given nuclear configuration.

Figure 12 illustrates a series of NAD terms calculated by *Columbus*. The label d/dn is shorthand for the derivative coupling term with respect to the coordinate n:  $\langle \varphi_i | \frac{\partial}{\partial n} \varphi_j \rangle$ .

The slice is the same as previously examined:  $R=5.0$  and  $r=1.402$  bohr. Note that for  $\gamma=4\pi/20, 5\pi/20$ , and  $6\pi/20$  the all of the terms take a sharp dive across the axis. If it is assumed that these three points have been calculated with a -1 phase shift, we can correct them with a simple sign adjustment. Figure 13 shows the same NAD terms with the phase correction made. *Columbus* calculated the points marked, whereas the lines are interpolations on those points. We could have chosen the exact opposite situation and assumed that those three points were correct and all the others were flipped. The result would be the same, only inverted about the axis. The total phase factor is irrelevant so long as it is the same for all measurements. We cannot, however, choose to correct some

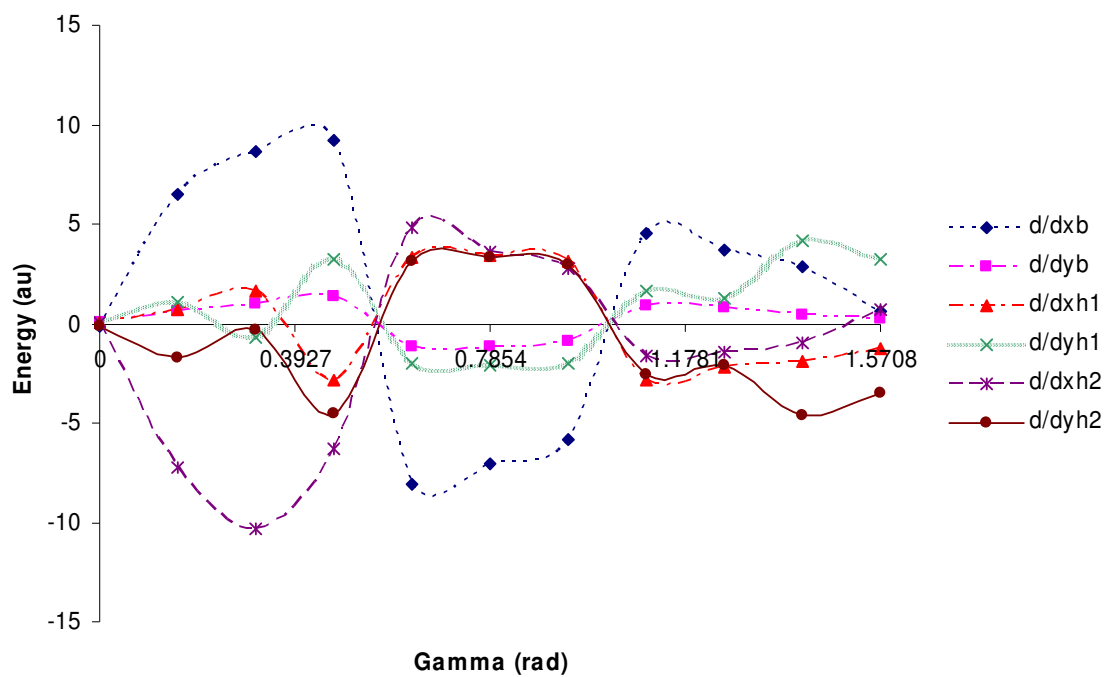


Figure 12. Cartesian NAD Terms from Columbus with Uncorrected Phase

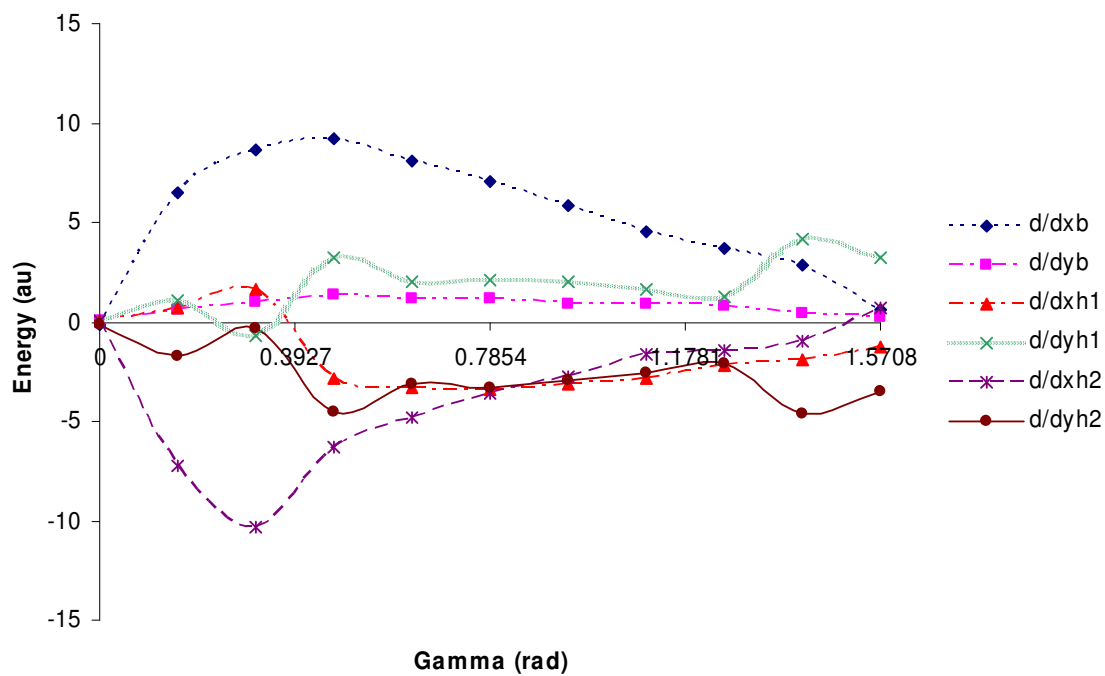


Figure 13. Cartesian NAD terms from Columbus with Corrected Phase

of the NAD terms at a given nuclear configuration and not others. For instance in Figure 13 it would be tempting to correct the  $d/dx_{h1}$  and  $d/dy_{h1}$  terms alone at  $\gamma = \pi/10$ . This is forbidden without flipping the other four terms as well, and by examining the  $d/dx_b$  and  $d/dx_{h2}$  terms we can judge that inversion would not be prudent. Figure 14 shows the NAD terms for the same slice of potential energy surface as calculated by Dr. Yarkony in

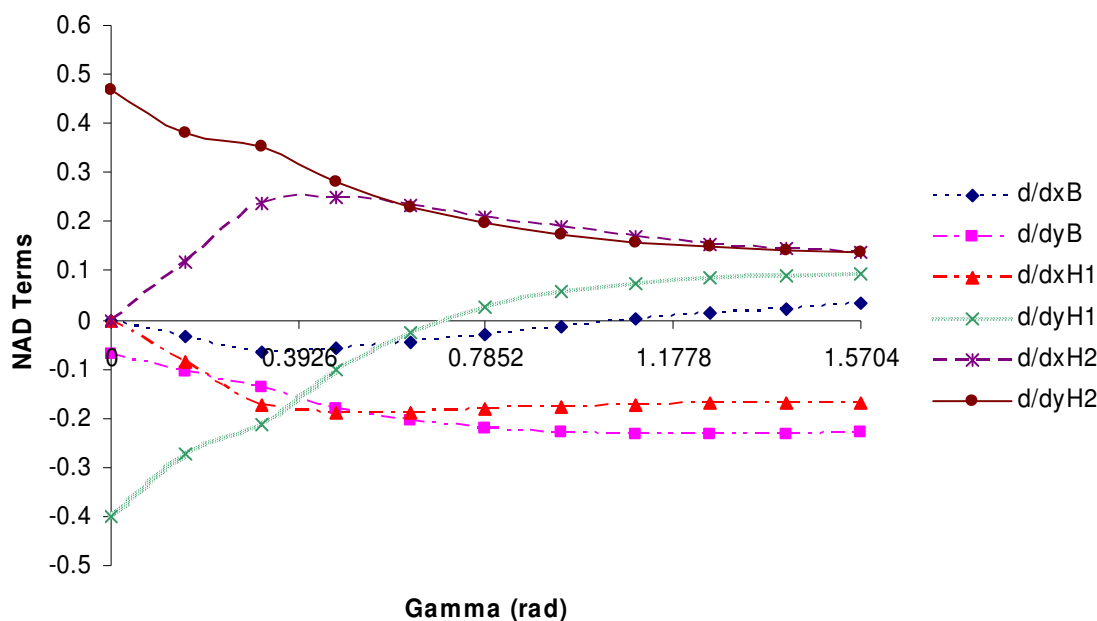


Figure 14. Cartesian NAD Terms from Brooklyn with Corrected Phase

*Brooklyn* after a corrected phase factor has been applied. Unlike for the potential energy surface calculations, the NAD term outputs from *Columbus* and *Brooklyn* are not close at all. Not only do they have different shapes, but they differ by an order of magnitude. Unfortunately at this time we are unable to verify the NAD terms from *Brooklyn* by our own calculations in *Columbus*, which was to be the first exploration in finding the error in previous calculations. The negative result from *Columbus* is probably a result of

running it with faulty input files. However, correction of the error in the second exploration (the conversion of Cartesian to Jacobi derivative coupling terms) produced results that agreed with theory; thus the NAD terms from *Brooklyn* are demonstrably correct.

### **The Jacobi Transformation**

Let us now examine the NAD terms in Jacobi coordinates. With six Cartesian coordinates we are able to define any possible configuration of  $B+H_2$  within the plane. When creating inputs for *Columbus* and *Brooklyn* in Figure 5 we were able to restrict the placement of the system in the plane to minimize the number of Cartesian coordinates required to specify an internal geometry. This restriction was acceptable for the purposes of simplifying inputs because the potential energy surfaces and NAD terms only depend on internal geometry; that is, they only depend on the relative positions of the atoms to each other, not where they are with respect to the origin.

In order to convert from one coordinate system to another, we need to lift the restriction of how the system is oriented with respect to the origin. . The usual Jacobi coordinates are internal; they orient the atoms with respect to each other but specify no information whatsoever about where in the plane the system is found. We need to augment our three Jacobi coordinates with an overall displacement and an overall rotation. We choose the center of mass of the system as the point to measure displacement, although any point that is fixed in the center of mass frame of reference will yield the same result. At this point the choice of rotation angle reference,  $\omega$ , is arbitrary inasmuch as it is independent of the other five Jacobi coordinates. The choice of Dr. Yarkony is

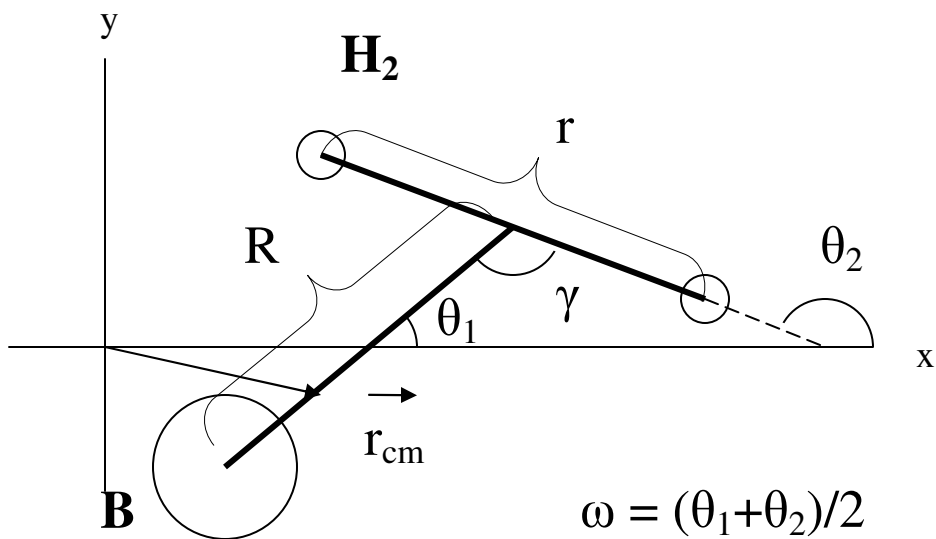


Figure 15. The Six Jacobi Coordinates

illustrated in Figure 15. His  $\omega$  is an average of  $\theta_1$  and  $\theta_2$  (Weeks, 2004). This arrangement also allows  $\gamma$  to be alternatively defined as  $\theta_2 - \theta_1$ . Thus the six Jacobi coordinates are:  $R$ ,  $r$ ,  $\gamma$ ,  $x_{cm}$ ,  $y_{cm}$ , and  $\omega$ . These Jacobi coordinates are independent; that is, any one can be changed without forcing any of the others to change. For the sake of being arbitrary, one could just as easily have chosen either  $\theta_1$  or  $\theta_2$  as the reference of rotation, as either one is also independent of the other five coordinates. But as we will show, in order to separate the internal and external Hamiltonians, the choice of reference angle must be specifically  $\omega = \theta_1$ ; this was the cause of error in the coupling angles calculated from the Jacobi NAD terms. The six Cartesian coordinates are:  $x_B$  and  $y_B$ , the position of boron;  $x_{H1}$  and  $y_{H1}$  the position of one of the hydrogens; and  $x_{H2}$  and  $y_{H2}$  the position of the other hydrogen.



The output of *Brooklyn* or *Columbus* gives us the Cartesian NAD terms; but mixing them all to come up with Jacobi derivatives is a formidable task. A Jacobi derivative coupling term is extracted from the Cartesian derivative coupling terms by:

$$\left\langle \varphi_i \left| \frac{d}{dR} \varphi_j \right. \right\rangle = \left\langle \varphi_i \left| \frac{\partial x_B}{\partial R} \frac{\partial}{\partial x_B} \varphi_j + \frac{\partial y_B}{\partial R} \frac{\partial}{\partial y_B} \varphi_j + \frac{\partial x_{H1}}{\partial R} \frac{\partial}{\partial x_{H2}} \varphi_j + \frac{\partial y_{H1}}{\partial R} \frac{\partial}{\partial y_{H1}} \varphi_j + \frac{\partial x_{H2}}{\partial R} \frac{\partial}{\partial x_{H2}} \varphi_j + \frac{\partial y_{H2}}{\partial R} \frac{\partial}{\partial y_{H2}} \varphi_j \right. \right\rangle \quad (42)$$

or

$$\begin{aligned} \left\langle \varphi_i \left| \frac{d}{dR} \varphi_j \right. \right\rangle = & \frac{\partial x_B}{\partial R} \left\langle \varphi_i \left| \frac{\partial}{\partial x_B} \varphi_j \right. \right\rangle + \frac{\partial y_B}{\partial R} \left\langle \varphi_i \left| \frac{\partial}{\partial y_B} \varphi_j \right. \right\rangle + \frac{\partial x_{H1}}{\partial R} \left\langle \varphi_i \left| \frac{\partial}{\partial x_{H1}} \varphi_j \right. \right\rangle + \\ & \frac{\partial y_{H1}}{\partial R} \left\langle \varphi_i \left| \frac{\partial}{\partial y_{H1}} \varphi_j \right. \right\rangle + \frac{\partial x_{H2}}{\partial R} \left\langle \varphi_i \left| \frac{\partial}{\partial x_{H2}} \varphi_j \right. \right\rangle + \frac{\partial y_{H2}}{\partial R} \left\langle \varphi_i \left| \frac{\partial}{\partial y_{H2}} \varphi_j \right. \right\rangle \end{aligned} \quad (43)$$

where R can represent any of the Jacobi coordinates. Inspection of equation (42) reveals that this equality arises from the chain rule for partial derivatives. Equation (43) reveals that this is equal to a product of Cartesian derivative coupling terms and derivatives of the Cartesian coordinates with respect to the Jacobi coordinate in question. Given the vectors

$$R = \left( x_b - \frac{x_{H1} + x_{H2}}{2}, y_b - \frac{y_{H1} + y_{H2}}{2} \right) \quad (44)$$

and

$$r = (x_{H2} - x_{H1}, y_{H2} - y_{H1}), \quad (45)$$

the Jacobi coordinates in terms of the Cartesians are

$$R = |\vec{R}|, \quad (46)$$

$$r = |\vec{r}|, \quad (47)$$

$$x_{cm} = \frac{1}{m_B + m_{H1} + m_{H2}} \cdot (m_B \cdot x_B + m_{H1} \cdot x_{H1} + m_{H2} \cdot x_{H2}), \quad (48)$$

$$y_{cm} = \frac{1}{m_B + m_{H1} + m_{H2}} \cdot (m_B \cdot y_B + m_{H1} \cdot y_{H1} + m_{H2} \cdot y_{H2}), \quad (49)$$

$$\theta_1 = \arccos\left(\frac{\vec{r}_x}{|\vec{r}|}\right), \quad (50)$$

and

$$\theta_2 = \arccos\left(-\frac{\vec{R}_x}{|\vec{R}|}\right), \quad (51)$$

It is very difficult if not impossible to analytically solve for the derivatives in equation (43) because the above transformation is not invertible. Fortunately the reverse operation, getting the derivatives of the Jacobi coordinates with respect to the Cartesian coordinates is fairly straight forward. The matrix that contains all the partial derivatives of one set of coordinates with respect to another set is called the *Jacobian*. The Jacobian for the Cartesian-to-Jacobi operation looks like

$$\begin{pmatrix} \frac{\partial x_B}{\partial r} & \frac{\partial y_B}{\partial r} & \frac{\partial x_{H1}}{\partial r} & \frac{\partial y_{H1}}{\partial r} & \frac{\partial x_{H2}}{\partial r} & \frac{\partial y_{H2}}{\partial r} \\ \frac{\partial x_B}{\partial x_B} & \frac{\partial y_B}{\partial y_B} & \frac{\partial x_{H1}}{\partial x_{H1}} & \frac{\partial y_{H1}}{\partial y_{H1}} & \frac{\partial x_{H2}}{\partial x_{H2}} & \frac{\partial y_{H2}}{\partial y_{H2}} \\ \frac{\partial R}{\partial x_B} & \frac{\partial R}{\partial y_B} & \frac{\partial R}{\partial x_{H1}} & \frac{\partial R}{\partial y_{H1}} & \frac{\partial R}{\partial x_{H2}} & \frac{\partial R}{\partial y_{H2}} \\ \frac{\partial \gamma}{\partial x_B} & \frac{\partial \gamma}{\partial y_B} & \frac{\partial \gamma}{\partial x_{H1}} & \frac{\partial \gamma}{\partial y_{H1}} & \frac{\partial \gamma}{\partial x_{H2}} & \frac{\partial \gamma}{\partial y_{H2}} \\ \frac{\partial \omega}{\partial x_B} & \frac{\partial \omega}{\partial y_B} & \frac{\partial \omega}{\partial x_{H1}} & \frac{\partial \omega}{\partial y_{H1}} & \frac{\partial \omega}{\partial x_{H2}} & \frac{\partial \omega}{\partial y_{H2}} \\ \frac{\partial x_{cm}}{\partial x_B} & \frac{\partial x_{cm}}{\partial y_B} & \frac{\partial x_{cm}}{\partial x_{H1}} & \frac{\partial x_{cm}}{\partial y_{H1}} & \frac{\partial x_{cm}}{\partial x_{H2}} & \frac{\partial x_{cm}}{\partial y_{H2}} \\ \frac{\partial y_{cm}}{\partial x_B} & \frac{\partial y_{cm}}{\partial y_B} & \frac{\partial y_{cm}}{\partial x_{H1}} & \frac{\partial y_{cm}}{\partial y_{H1}} & \frac{\partial y_{cm}}{\partial x_{H2}} & \frac{\partial y_{cm}}{\partial y_{H2}} \end{pmatrix}. \quad (52)$$

This matrix dotted into a vector containing the Cartesian derivative coupling terms leads to six values that have the form of the right-hand-side of equation (43):

$$\begin{pmatrix} \frac{\partial x_B}{\partial r} & \frac{\partial y_B}{\partial r} & \dots \\ \frac{\partial x_B}{\partial R} & \frac{\partial y_B}{\partial R} & \dots \\ \vdots & \vdots & \ddots \end{pmatrix} \bullet \begin{pmatrix} \left\langle \varphi_i \left| \frac{\partial}{\partial x_B} \varphi_j \right\rangle \right\rangle \\ \left\langle \varphi_i \left| \frac{\partial}{\partial y_B} \varphi_j \right\rangle \right\rangle \\ \vdots \end{pmatrix} = \begin{pmatrix} \frac{\partial x_B}{\partial r} \left\langle \varphi_i \left| \frac{\partial}{\partial x_B} \varphi_j \right\rangle + \frac{\partial y_B}{\partial r} \left\langle \varphi_i \left| \frac{\partial}{\partial y_B} \varphi_j \right\rangle + \dots \\ \frac{\partial x_B}{\partial R} \left\langle \varphi_i \left| \frac{\partial}{\partial x_B} \varphi_j \right\rangle + \frac{\partial y_B}{\partial R} \left\langle \varphi_i \left| \frac{\partial}{\partial y_B} \varphi_j \right\rangle + \dots \\ \vdots \end{pmatrix} \quad (53)$$

The Jacobian for Jacobi-to-Cartesian conversion can be obtained by:

$$\begin{pmatrix} \frac{\partial x_B}{\partial r} & \frac{\partial y_B}{\partial r} & \dots \\ \frac{\partial x_B}{\partial R} & \frac{\partial y_B}{\partial R} & \dots \\ \vdots & \vdots & \ddots \end{pmatrix} = \begin{pmatrix} \frac{\partial r}{\partial x_B} & \frac{\partial R}{\partial x_B} & \dots \\ \frac{\partial r}{\partial y_B} & \frac{\partial R}{\partial y_B} & \dots \\ \vdots & \vdots & \ddots \end{pmatrix}^{-1} \quad (54)$$

(Weeks, 2004)

where the  $\partial R / \partial x_i$  are known analytically from the  $R=R(x_i)$  transformation in equations (46)-(51). Careful consideration shows that the product of these matrices is indeed the identity matrix, which confirms that going from Cartesian to Jacobi to Cartesian or vice versa is an identity operation and should leave the coordinates unchanged. It then becomes a simple matter of linear algebra to use this new Jacobian in conjunction with the Cartesian NAD terms to come up with the Jacobi NAD terms as per equation (43). Figure 16 shows the NAD terms from Figure 13 (those calculated by *Columbus*) after having been converted to Jacobi coordinates. Notice how erratic the angular derivatives are ( $d/d\gamma$  and  $d/d\omega$ ). Figure 17 shows the NAD terms from Figure 14 (those calculated by *Brooklyn*) after having been converted to Jacobi coordinates. Note that all the NAD

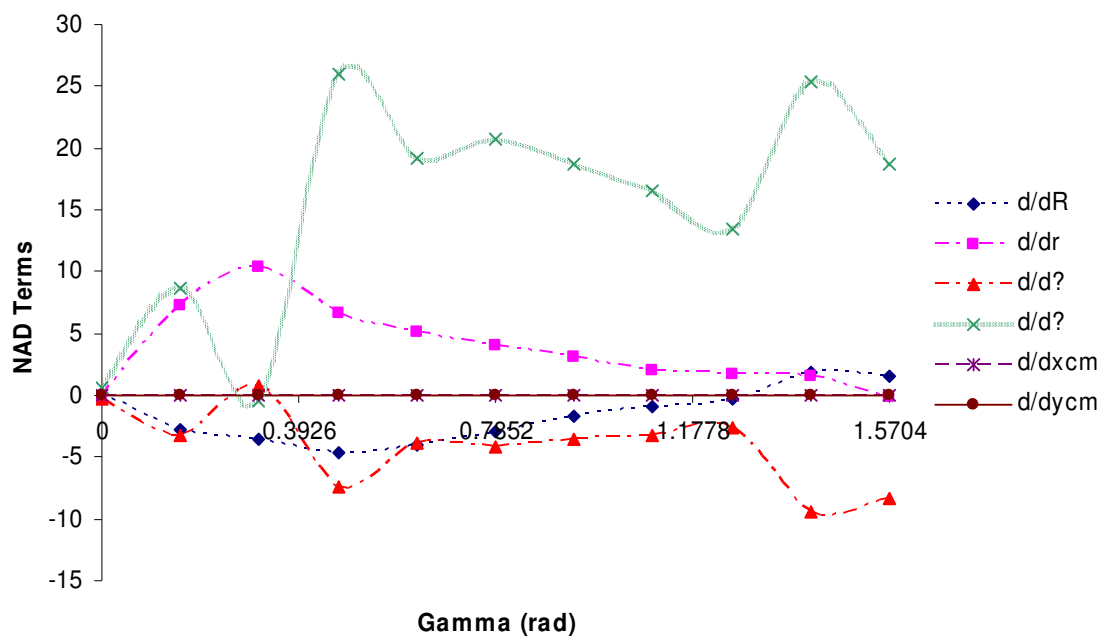


Figure 16. Jacobi NAD Terms from Columbus

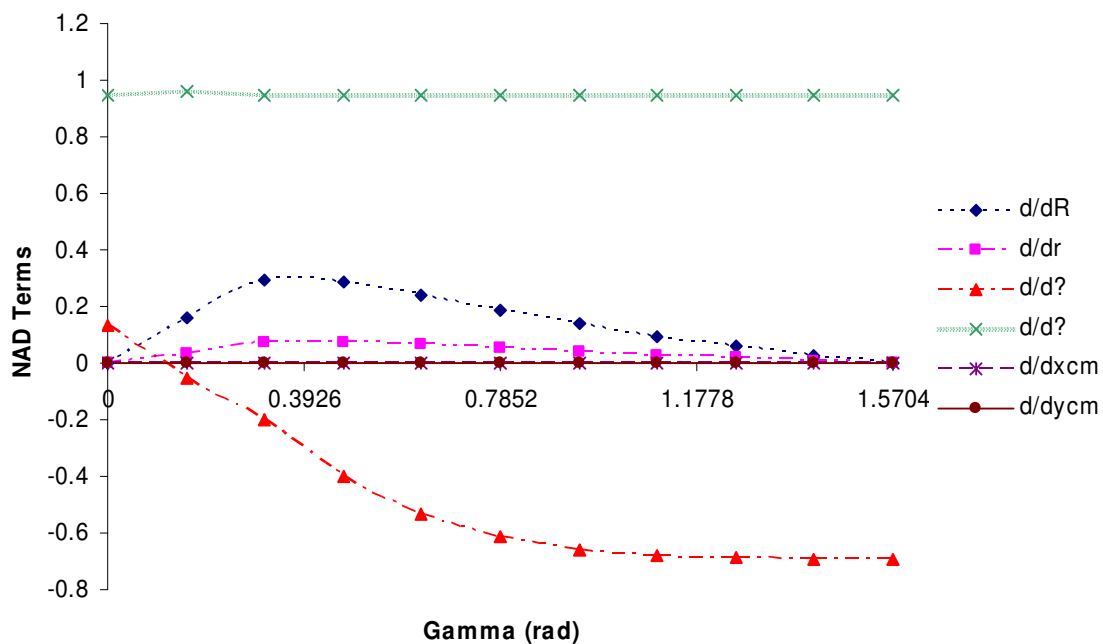


Figure 17. Jacobi NAD Terms from Brooklyn

terms change smoothly across the energy curve slice, especially the angular terms. Note also the much smaller scale that the *Brooklyn* NAD terms take on. Keep in mind that these Jacobi NAD terms were calculated with Dr. Yarkony's  $\omega$  from Figure 15, so they are not necessarily correct (specifically the  $d/d\gamma$  term). Initial calculation using these values led to the incorrect coupling angle as the next section will illustrate.

### Calculating the Coupling Angle

The derivative coupling terms we have calculated are used to create the coupling angle  $\Theta(\mathbf{R})$  in equation (37), which is then used to form the rotation matrix in equation (24). This rotation matrix then diagonalizes the kinetic energy operator and mixes the potential energy surfaces in the potential energy operator, placing them in the diabatic representation. Because the integral in equation (37) is path independent, we can choose to integrate from an arbitrary starting point through the derivative coupling terms to the point  $(\mathbf{R}, r, \gamma)$  in straight lines parallel to the axes (See Figure 18). This line integral can

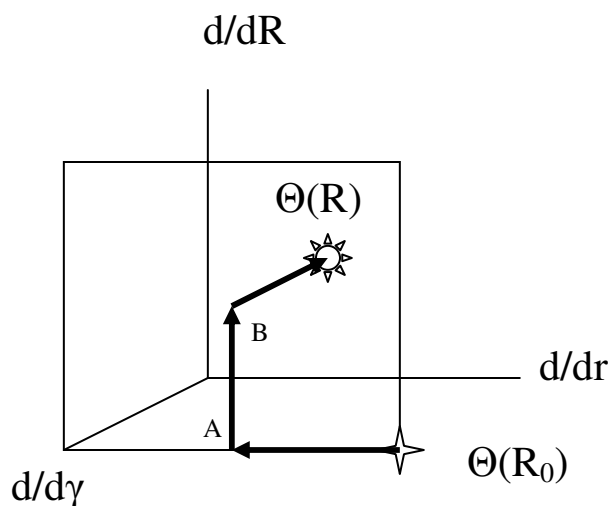


Figure 18. Path Integral to Calculate  $\Theta(\mathbf{R})$  in NAD-Term Space

be made even simpler by choosing to place the starting point for the integration in the plane  $\gamma = \pi/2$ . Notice in Figure 17 that the NAD terms with respect to  $r$  and  $R$  are nearly zero at  $\gamma = \pi/2$ . This is true for all values of  $R$  and  $r$ . Thus the integral from  $\Theta(\mathbf{R}_0)$  to A and A to B is negligible, and the entire integral is equal to the integral from B to  $\Theta(\mathbf{R})$ . This implies that  $\Theta(\mathbf{R})$  need only be integrated along  $\gamma$  (Weeks, 2004).

In his work on the  $B+H_2$  system with hydrogen at its equilibrium distance, Alexander calculated that whether the energy eigenvalues of the electronic Hamiltonian were positive or negative would depend on how close the hydrogens came to either end of the antisymmetric boron atomic p-orbital (1993:6018). Recall that these energy eigenvalues form the potential energy surfaces for the nuclear Hamiltonian. If the

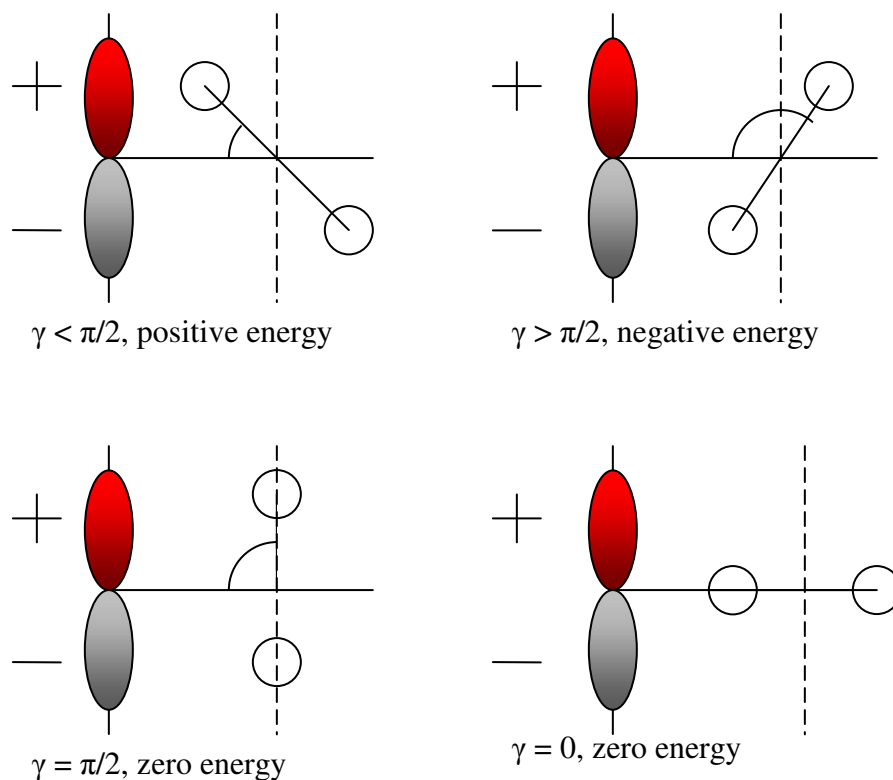


Figure 19. How  $\gamma$  Affects Electronic Eigenvalues

hydrogen swings closer to the positive lobe there is a repulsion and hence a positive energy. If it swings closer to the other lobe the opposite is true (see Figure 19). Since the potential energy surfaces must be continuous, this implies that in the collinear configuration and in the “T” configuration all the surfaces must go through zero. Alexander also derived that the off-diagonal (coupling) potential energy surface would be related to the coupling angle by:

$$E_{12} = \sin(\Theta(R))\cos(\Theta(R)) \cdot (E_1 - E_2) \quad (1993:6020). \quad (55)$$

In order for the surface to go to zero, this implies that  $\Theta(\mathbf{R})$  must go to 0 or  $\pi/2$  at  $\gamma = \pi/2$  and  $\gamma = 0$ . Because we put the arbitrary starting point of the integral at  $\gamma = \pi/2$ ,  $\Theta(\mathbf{R}, r, \pi/2)$  will always be equal to zero. Figure 20 shows Alexander’s calculation of coupling angle as a function of Jacobi angle. For below values of about  $R = 6.5$  the line integral goes back to zero and for values above it goes to  $\pi/2$ , as shown in Figure 20. The  $\gamma$  NAD

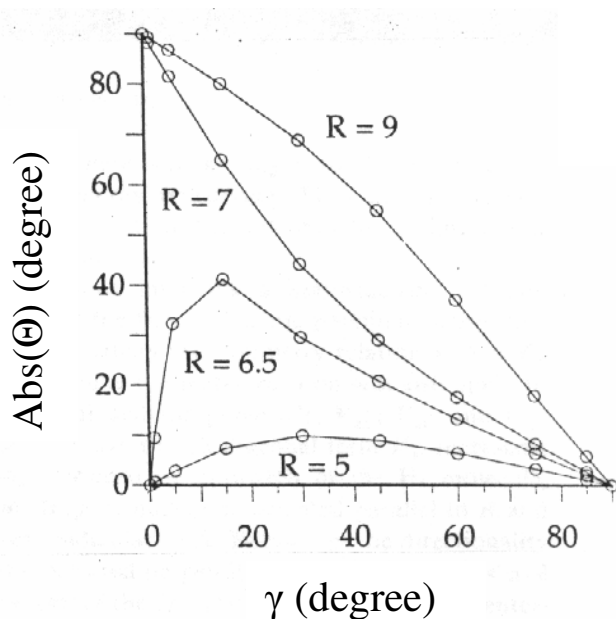


Figure 20. Alexander's Calculation of the Coupling Angle (1993:6019)

term as calculated in *Brooklyn* for the  $R=5$ ,  $r=1.402$  slice of the energy surface is shown in Figure 21 (this is extracted from Figure 17). For most of the slice the NAD term is negative, with only a small portion of the curve near zero being positive. The result of

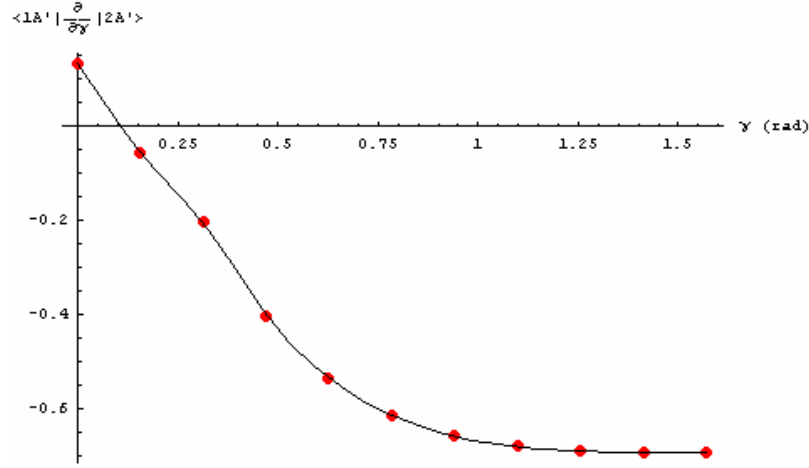


Figure 21.  $\gamma$  NAD Terms from Brooklyn

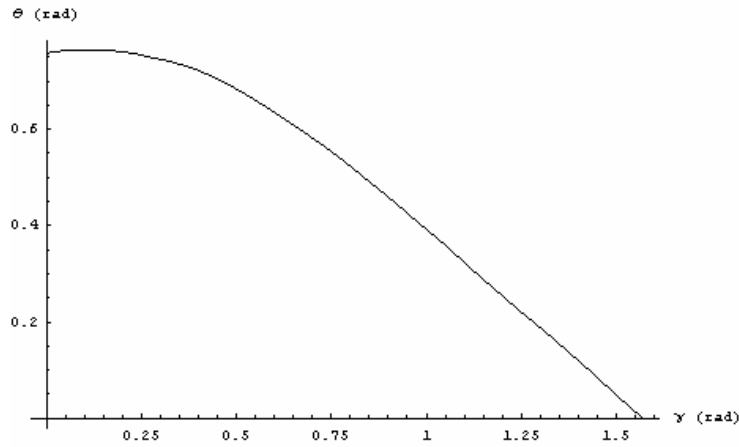


Figure 22. Coupling Angle from Brooklyn NAD Terms

the line integral across this slice is shown in Figure 22; the value approaches neither 0 nor  $\pi/2$  (this plot is actually the absolute value of the line integral for the sake of comparing with Alexander's data). This disagreement with theory implies that either the derivative



coupling terms produced by Brooklyn are wrong or the method of transforming them to Jacobi coordinates is wrong.

### Origin Dependency

Recall that when we oriented the system in the plane with Jacobi coordinates, we specified the angle  $\omega = (\theta_1 + \theta_2)/2$ , but there were several choices of angles that were independent of the other five Jacobi coordinates. Figure 23 shows the Jacobi NAD terms calculated with  $\omega = \theta_1$ . Compare this figure with Figure 17, which was calculated with  $\omega = (\theta_1 + \theta_2)/2$ . All the derivative coupling terms are exactly the same with the exception of the  $\gamma$  term. Even so the  $\gamma$  term appears to have the same line shape, but the terms are offset by a common constant (0.5). Clearly by choosing different but equally valid

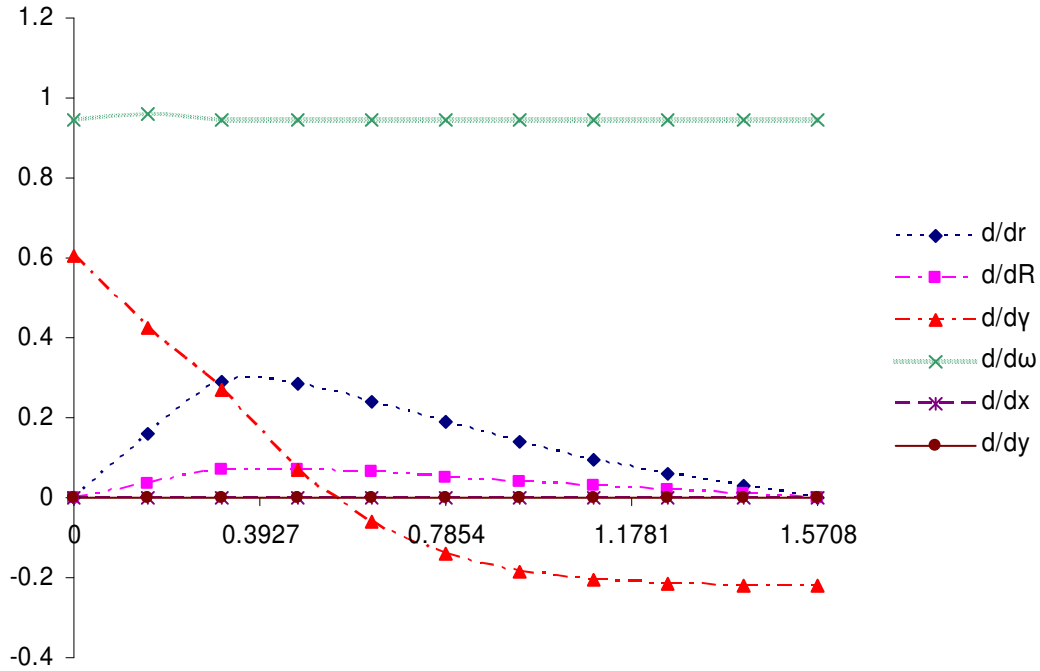


Figure 23. Jacobi NAD Terms from Brooklyn,  $\omega = \theta_1$

coordinate systems we affect some of the derivative coupling terms. This contingency on the choice of coordinates is known as an *origin dependency*.

Origin dependency is best understood by the following example. Consider a linear system of two masses as in Figure 24. We can construct two separate coordinate

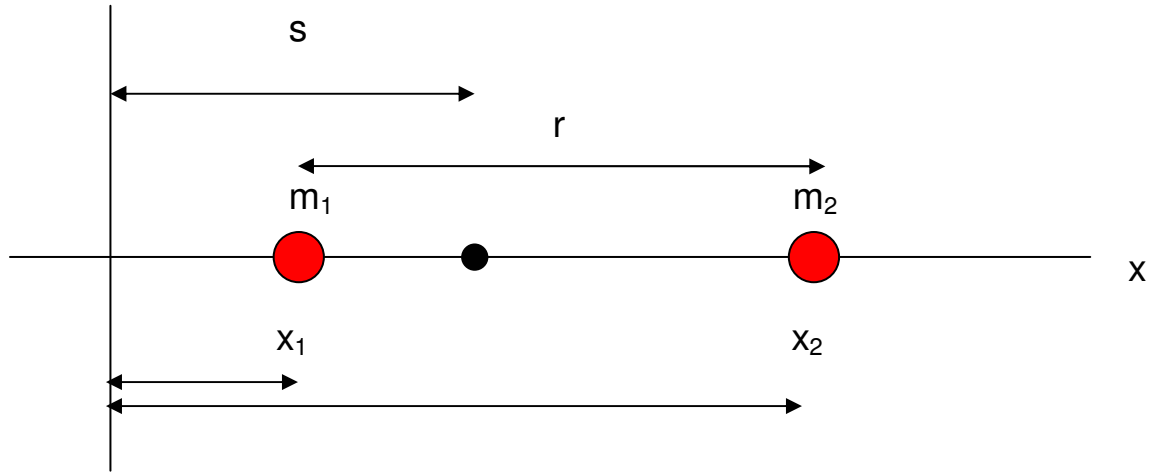


Figure 24. Simple Linear System

systems to describe their positions. The Cartesian coordinate set describes the system as  $(x_1, x_2)$  where  $x_1$  is the distance of mass  $m_1$  from the origin and  $x_2$  is the distance of mass  $m_2$  from the origin. The second system, which might be dubbed the center-of-mass coordinate set describes the system as  $(r, s)$  where  $r$  is the distance between the masses and  $s$  is the distance from the origin to some point relative to the positions of the two masses. If  $s$  is chosen such that  $s = m_1 \cdot x_1 + m_2 \cdot x_2$  then  $s$  is the distance to the center of mass, but in general the center-of-mass set is related to the Cartesian set by:

$$r = x_2 - x_1 \quad (56)$$

and

$$s = a * x_1 + b * x_2. \quad (57)$$

If we express this relationship in matrix form,

$$\begin{pmatrix} s \\ r \end{pmatrix} = \begin{pmatrix} a & b \\ -1 & 1 \end{pmatrix} \bullet \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} \quad (58)$$

we can easily invert it in order to find the Cartesian set in terms of the center-of-mass set:

$$\begin{pmatrix} x_1 \\ x_2 \end{pmatrix} = \frac{1}{a+b} \begin{pmatrix} 1 & -b \\ 1 & a \end{pmatrix} \bullet \begin{pmatrix} s \\ r \end{pmatrix}. \quad (59)$$

From this we can extract the Jacobian:

$$Jacobian \equiv \begin{pmatrix} \frac{\partial x_1}{\partial s} & \frac{\partial x_2}{\partial s} \\ \frac{\partial x_1}{\partial r} & \frac{\partial x_2}{\partial r} \end{pmatrix} = \begin{pmatrix} \frac{1}{a+b} & \frac{1}{a+b} \\ \frac{-b}{a+b} & \frac{a}{a+b} \end{pmatrix}. \quad (60)$$

Now suppose we have the derivative of some function,  $\psi$  with respect to the Cartesian coordinates, but we want its derivative with respect to the center-of-mass coordinates.

We just dot the Jacobian into the derivatives (compare equation (43)):

$$\begin{pmatrix} \frac{\partial \Psi}{\partial s} \\ \frac{\partial \Psi}{\partial r} \end{pmatrix} = \begin{pmatrix} \frac{\partial x_1}{\partial s} & \frac{\partial x_2}{\partial s} \\ \frac{\partial x_1}{\partial r} & \frac{\partial x_2}{\partial r} \end{pmatrix} \bullet \begin{pmatrix} \frac{\partial \Psi}{\partial x_1} \\ \frac{\partial \Psi}{\partial x_2} \end{pmatrix}. \quad (61)$$

The derivatives evaluate to

$$\frac{\partial \Psi}{\partial s} = \frac{1}{a+b} \frac{\partial \Psi}{\partial x_1} + \frac{1}{a+b} \frac{\partial \Psi}{\partial x_2} \quad (62)$$

and

$$\frac{\partial \Psi}{\partial r} = \frac{-b}{a+b} \frac{\partial \Psi}{\partial x_1} + \frac{a}{a+b} \frac{\partial \Psi}{\partial x_2}. \quad (63)$$

As long as the sum of a and b are the same, the derivative with respect to s, the external coordinate, remains the same; but the derivative with respect to r, the internal coordinate, varies as the ratio of a to b varies.

This simple example helps to explain the relationship between the  $\omega$  and the  $\gamma$  NAD terms. The internal angular coordinate,  $\gamma$ , was defined as  $\theta_2 - \theta_1$  whereas the external angular coordinate,  $\omega$ , was defined as  $a\theta_1 + b\theta_2$ . As long as  $a+b = 1$  the  $\omega$  NAD terms remained the same, while the  $\gamma$  NAD terms varied with the ratio of a to b. This implies that the choice of a and b is not arbitrary when calculating the  $\gamma$  NAD term. Part of the reason that  $\omega = (\theta_1 + \theta_2)/2$  was not discounted immediately upon finding the error in the coupling angle was that the value of the  $d/d\omega$  term, which is a measure of angular momentum, was compared to and found matching the angular momentum calculated using other methods and it was assumed that all other NAD terms must also be correct.

The correct choice of a and b to extract the correct derivative coupling terms and consequently the correct coupling angle is buried in another form of the Hamiltonian which is generalized for use in three dimensions:

$$\hat{H} = \frac{\hat{p}_R^2}{2\mu_{B,H_2}} + \frac{\hat{p}_r^2}{2\mu_{H_2}} + \frac{\hat{j}^2}{2\mu_{H_2} r^2} + \frac{\hat{L}^2}{2\mu_{B,H_2} R^2} + \hat{V}_{el} + \hat{V}_{so} \quad (64)$$

where the first term is the linear momentum of the boron with respect to the hydrogen, the second term is the vibrational motion of the hydrogen molecule, the third is the angular momentum of the hydrogen, the fourth is the angular momentum of the system, the fifth is the potential due to the electrons, and the sixth is a spin-orbit term (Niday, 1999:20). The third term in the Hamiltonian is associated with  $\gamma$  and the fourth term is associated

with  $\omega$ . Coming to this form of the Hamiltonian in which the internal and external angular momenta are separated required using the Euler angles as part of the coordinate system. Since we are restricting our system to a plane we need not use all of the Euler angles; however, we still need one of them,  $\beta$ , to account for the system's rotation in the plane. The Euler angle  $\beta$  is the angle  $\theta_1$  from Figure 15. Thus in order to successfully separate the Hamiltonian to arrive at the correct coupling angles, we must set  $a$  to 1 and  $b$  to 0; that is,  $\omega = \theta_1$ . Figure 25 shows the  $\gamma$  NAD terms for  $R = 5$ ,  $r = 1.402$ , and the resultant coupling angle after setting  $\omega$  to equal  $\theta_1$ . In agreement with Millard Alexander's

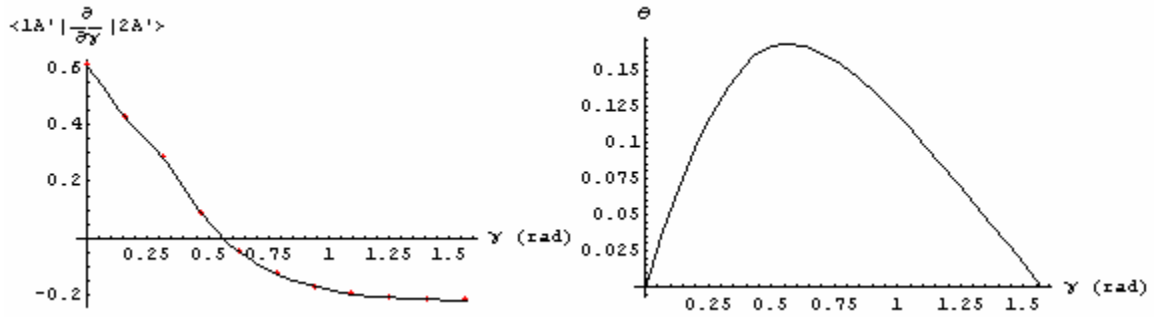


Figure 25.  $\gamma$  NAD Terms and Line Integral After Effecting Rotation

data, the coupling angle now goes to zero at  $\gamma = 0$ . Figure 26 shows the line integrals after rotation for a variety of lengths of  $R$ . Table 1 compares their value at  $\gamma = 0$  to 0 or  $\pi/2$ . Since these coupling angles behave almost exactly as Alexander calculated, we can conclude that the derivative coupling terms given by *Brooklyn* are correct.

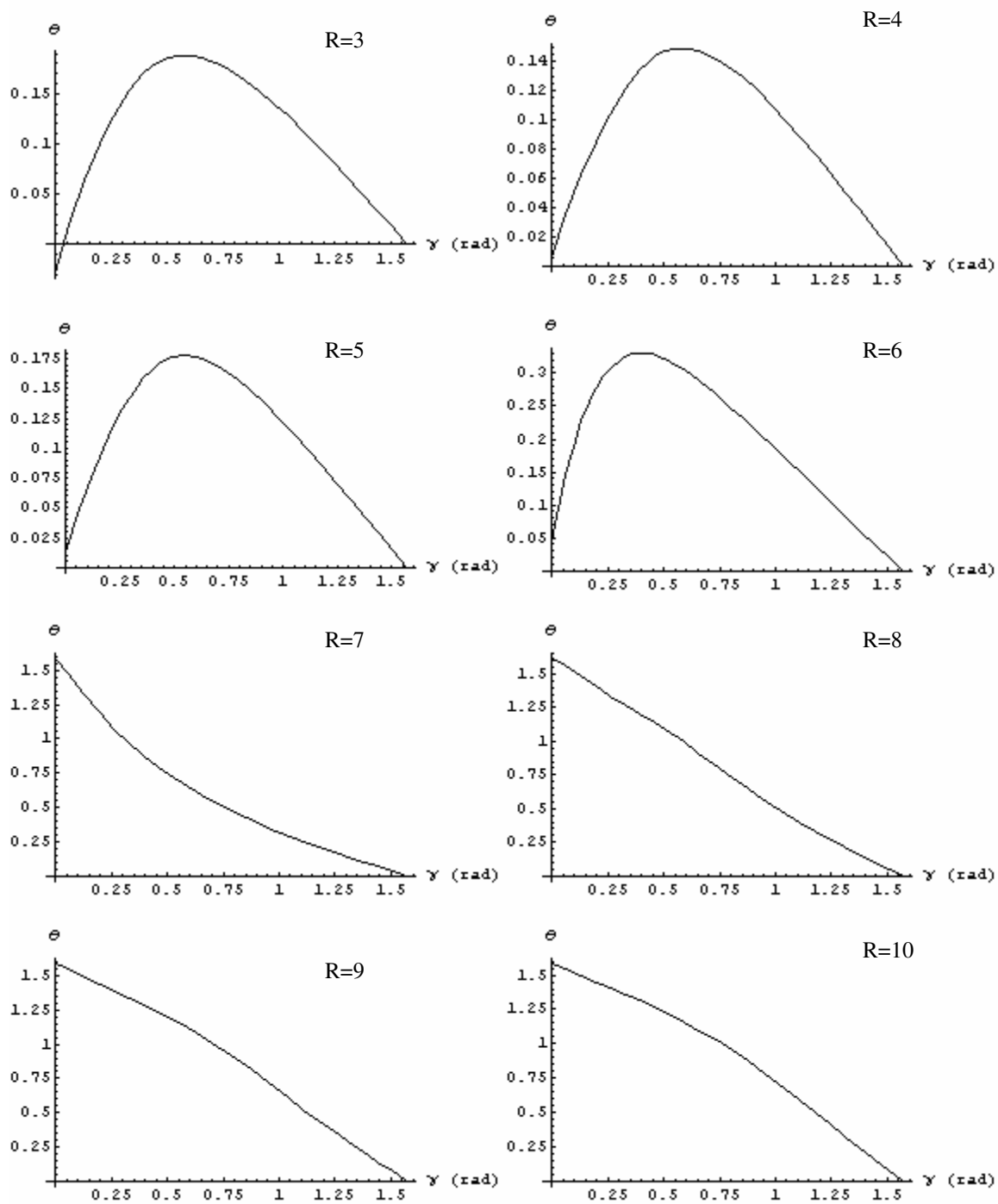


Figure 26. Coupling Angles After Rotation for Various R

**Table 1. Line Integrals Expected vs. Actual Values**

R	Expected (rad)	Actual (rad)	Difference (rad)
3	0	0.028819	-0.02882
4	0	0.006078	-0.00608
5	0	0.012663	-0.01266
6	0	0.04257	-0.04257
7	1.570796327	1.588636	-0.01784
8	1.570796327	1.619886	-0.04909
9	1.570796327	1.595284	-0.02449
10	1.570796327	1.587158	-0.01636

### Calculating the Non-Adiabatic Surfaces

Having verified the coupling angles we may now proceed to construct the non-adiabatic surfaces which we have sought. The coupling angle,  $\Theta(\mathbf{R})$  is used to construct the rotation matrix in equation (24). The rotation matrix is then applied to both the kinetic and potential energy operators as in equation (25). Rotation of the potential energy operator creates the diabatic potential energy operator:

$$\begin{bmatrix} 1A_b' & C_{2A'-1A'} & 0 \\ C_{1A'-2A'} & 2A_b' & 0 \\ 0 & 0 & 1A_b'' \end{bmatrix} = \begin{bmatrix} \cos(\Theta(R)) & \sin(\Theta(R)) & 0 \\ -\sin(\Theta(R)) & \cos(\Theta(R)) & 0 \\ 0 & 0 & 1 \end{bmatrix} \bullet \begin{bmatrix} 1A' & 0 & 0 \\ 0 & 2A' & 0 \\ 0 & 0 & 1A'' \end{bmatrix} \bullet \begin{bmatrix} \cos(\Theta(R)) & \sin(\Theta(R)) & 0 \\ -\sin(\Theta(R)) & \cos(\Theta(R)) & 0 \\ 0 & 0 & 1 \end{bmatrix}^{-1} \quad . (65)$$

The new diagonal terms are the diabatic energy surfaces, and only the  $1A''$  surface which did not mix remains the same. The off-diagonal terms are the coupling surface. Although not a proper surface, the coupling surface gives a measure of the likelihood that the  $1A'$  and  $2A'$  surfaces will couple; that is, that a wave function found on one will work its way onto the other.

Application of this method to the slices shown in Figure 11 results in the surfaces shown in Figure 27. This figure includes only the 1A' and 2A' surfaces since the 1A'' surface does not mix and is left as before in its adiabatic state. Once again these are two-

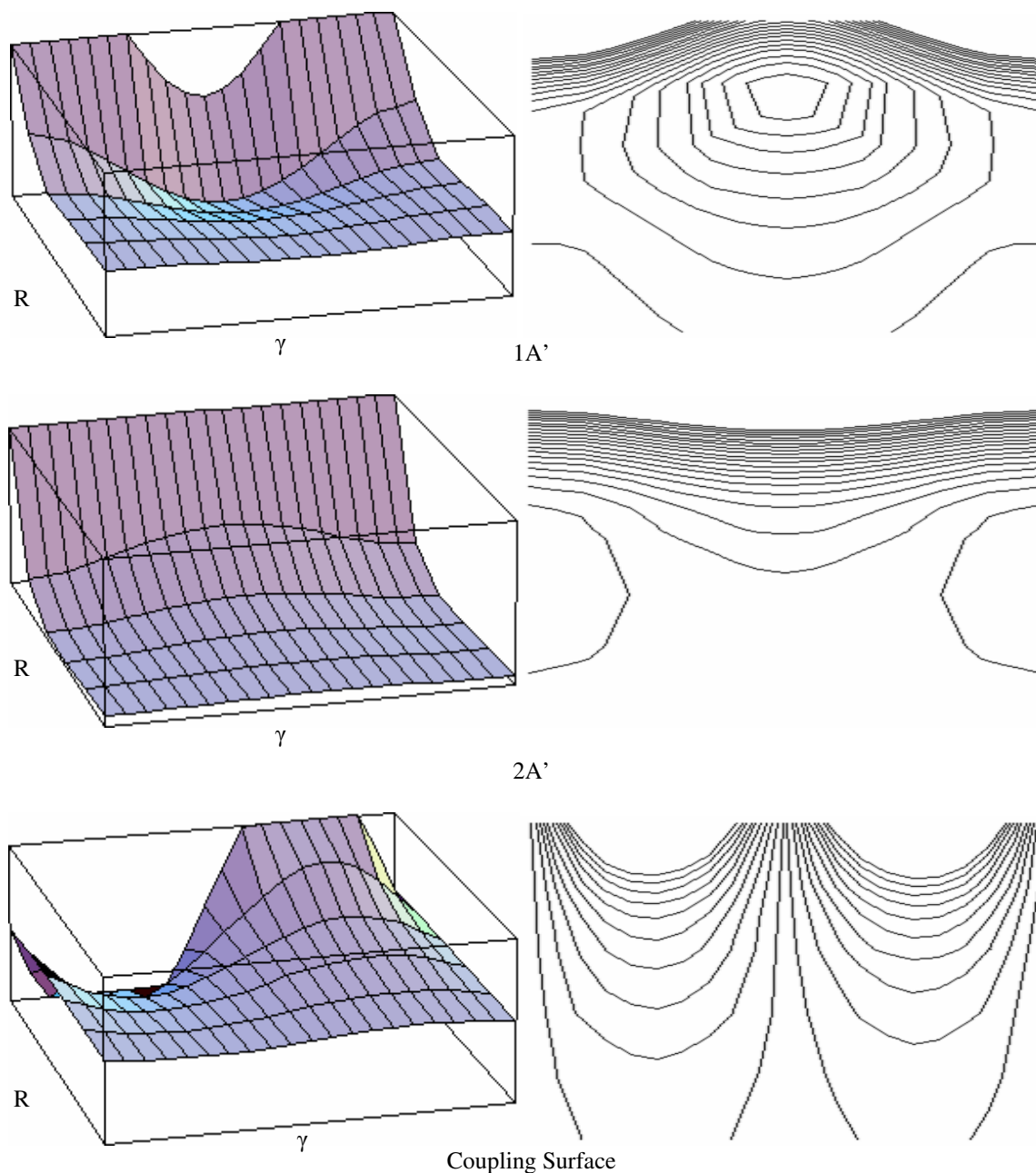


Figure 27. Surface and Contour Plots of the 1A' and 2A' Diabatic Surfaces and the Coupling Surface



dimensional slices of three-dimensional surfaces, the slice being taken at  $r = 1.402$  bohr. The first column has the surface plots and the second column has overhead contour plots. The  $1A'$  and  $2A'$  surfaces are plotted on the range of  $R = 5$  to  $10$  and  $\gamma = 0$  to  $\pi$ . To this figure we have also added the feature we had been missing from the adiabatic picture: the coupling surface. The coupling surface shows more coupling as  $R$  gets smaller and less as  $R$  gets larger. It also shows that at  $\gamma = \pi/2$  there is no coupling. This is significant because this is the region on the  $1A'$  surface where the potential well is deepest and the Van der Waals molecule, should it be formed, is most likely to be found. That implies that there is very little possibility of the molecule “leaking” out onto the antibonding  $2A'$  surface, which would seem to confirm that  $B+H_2$  is a good candidate for being a HEDM. However, should the hydrogen molecule rotate to the left or right with respect to the boron, the coupling becomes very large.

These surfaces can be compared to the surfaces that Alexander calculated and be found matching (1993; 6021-24). This too is significant because it means that the NAD terms calculated in *Brooklyn* by Dr. Yarkony are correct. Furthermore this verifies that the definition of  $\omega$  as the Euler angle  $\beta$  is correct and produces the correct coupling angle. This means that the balance of the surfaces for lengths of  $r$  different from the equilibrium distance can be mapped out with confidence using this method.

## IV. Conclusion

Adiabatic chemistry has been the staple of quantum chemistry for several decades. The Born-Oppenheimer approximation has made problems tractable on computers. Nevertheless, as computers become more capable and we demand more accuracy in our calculations of molecular wave functions and energy surfaces, diabatic chemistry or at least adiabatic/diabatic hybrid chemistry is becoming increasingly important. As it works its way into code and models we must be aware of the various problems associated with its implementation, like this origin dependency. Extreme care must be taken when calculating the coupling between non-adiabatic energy surfaces so that this origin dependency or one similar to it does not creep its way into the results and papers of unaware researchers.

As for this project, we can conclude that the derivative coupling terms created by *Brooklyn* are indeed correct. We have calculated a subset of the coupling angles and diabatic surfaces from these data and found them agreeing with the work of Millard Alexander. Follow-on projects will now be able to use the data to complete the full three-dimensional surfaces. These surfaces can then be used to construct the scattering matrix and characterize whether  $B+H_2$  can be used as a high energy density fuel.

On the subject of *Columbus* it is unfortunate that we were not able to create our own derivative coupling terms similar to those created by *Brooklyn*. Many man-hours were used to tweak *Columbus*' switches and knobs and, although progress was made, the right inputs could not be found. Hopefully with more contact and communication with the maintainers of *Columbus* future researchers in the Department of Physics in need of

derivative coupling terms will be able to master the code and create them according to their needs.

## Appendix A: The Scattering Matrix

The end of finding the non-adiabatic potential surfaces is making the scattering matrix. Because the scattering operator exists in linear momentum space crossed with linear momentum space, its matrix representation is dense and infinitely large. We can therefore only calculate a certain portion of the matrix around values we find most interesting. Further, we can only calculate the matrix in discrete steps and must interpolate the other values if we should need them.

The scattering problem begins by specifying  $|\Psi_{in}\rangle$  and  $|\Psi_{out}\rangle$ , the wave packets of the initial and final states, respectively (Niday, 1999:6). These states must then be propagated to their asymptotic limits, reactants to  $t = -\infty$  and products to  $t = \infty$  using the asymptotic Hamiltonian:

$$|\Psi_{in}^{Intermediate}\rangle = \exp\left\{-\frac{i\hat{H}_0 t}{\hbar}\right\}|\Psi_{in}\rangle \quad (66)$$

and

$$|\Psi_{out}^{Intermediate}\rangle = \exp\left\{-\frac{i\hat{H}_0 t}{\hbar}\right\}|\Psi_{out}\rangle. \quad (67)$$

These intermediate states are then taken from infinity and propagated toward interaction via the Hamiltonian created with the potential surfaces:

$$|\Psi_{+}\rangle = \exp\left\{-\frac{i\hat{H}t}{\hbar}\right\}|\Psi_{in}^{Intermediate}\rangle \quad (68)$$

and

$$|\Psi_{-}\rangle = \exp\left\{-\frac{i\hat{H}t}{\hbar}\right\}|\Psi_{out}^{Intermediate}\rangle. \quad (69)$$

The scattering matrix element is a “bridge” between these two states, so in order to calculate it, we must calculate a correlation between the two states:

$$C_{\gamma\gamma'}(t) = \left\langle \Psi_{-}^{\gamma'} \left| \exp\left\{-\frac{i\hat{H}t}{\hbar}\right\} \cdot \Psi_{+}^{\gamma} \right\rangle \quad (70)$$

where the reactants and products have now been indexed by  $\gamma$  and  $\gamma'$  to differentiate specific beginning and ending states. The scattering matrix operator element is then calculated as:

$$S_{\pm k_{\gamma}, \pm k_{\gamma'}}^{\gamma\gamma'} = \frac{\hbar/2\pi \sqrt{(|k_{\gamma'}| \cdot |k_{\gamma}|)}}{\sqrt{\mu_{\gamma}\mu_{\gamma'}} \eta_{-}^{*}(\pm k_{\gamma'}) \cdot \eta_{+}(\pm k_{\gamma})} \int_{-\infty}^{+\infty} dt \exp\left\{\frac{iEt}{\hbar}\right\} C_{\gamma\gamma'}(t). \quad (71)$$

where  $E$  is the total energy,  $k_{\gamma}$  is the relative momentum between reactants,  $k_{\gamma'}$  is the relative momentum between products,  $\eta_{\pm}(\pm k_{\gamma})$  are expansion coefficients used to construct the initial states, and  $\mu_{\gamma}$  are the reduced masses.

## Appendix B: The Many-Body Problem

Although we have traced the theory of non-adiabatic energy surfaces from beginning to end, we are unable to put it to use unless we actually calculate the electronic wave functions themselves.

The student of quantum mechanics is well acquainted with the derivation of hydrogenic orbitals. He has also been reminded time and time again by his professors that this two-body problem is the only one of its kind for which one can solve analytically the molecular wave functions. Even the addition of a single electron puts calculation of molecular wave functions squarely in the hands of the computer. In the B+H<sub>2</sub> system we have 10 bodies including nuclei and electrons. Fortunately we are not without help—a number of methods to iteratively approximate molecular wave functions are available.

### Hartree-Fock

The most basic way to determine molecular wave functions, and the method upon which more complicated models are based, is the Hartree-Fock method (Szabo, 1996:108-230). This method solves the Hartree-Fock eigenvalue equation,

$$\left( -\frac{1}{2}\nabla_i^2 - \sum_{\alpha} \frac{Z_{\alpha}}{r_{i\alpha}} + v^{HF}(i) \right) \chi(x_i) = \epsilon \chi(x_i) \quad (72)$$

where the  $v^{HF}$  is the average potential experienced by the  $i^{\text{th}}$  electron due to the other electrons. The quantity in parentheses is known as the Fock operator. By introducing this average interaction, the energy  $\epsilon$  is merely a sum of the individual orbital energies for each electron, and the wave function,  $\Psi$ , is a product of the hydrogenic type orbital of each electron:

$$\Psi(x_1, x_2 \dots x_n) = \chi_1(x_1) \chi_2(x_2) \dots \chi_n(x_n) \quad (73)$$

where  $\chi_i$  represents a spin orbital and  $x_i$  are the coordinates of a given electron. A spin orbital is the product of an atomic orbital and a spin function, which can be either up ( $\alpha(\omega)$ ) or down ( $\beta(\omega)$ ). This form of the wave function is not yet complete; it does not necessarily conform to the antisymmetry principle. This principle, which is born out of the Pauli Exclusion Principle, states that

$$\Psi(\dots x_i \dots x_j \dots) = -\Psi(\dots x_j \dots x_i \dots). \quad (74)$$

In order that  $\Psi$  obeys this principle, we introduce Slater Determinants, so that

$$\Psi(x_1, x_2 \dots x_n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \chi_1(x_1) & \chi_2(x_1) & \dots \\ \chi_1(x_2) & \chi_2(x_2) & \dots \\ \vdots & \vdots & \ddots \end{vmatrix} \quad (75)$$

These Slater Determinants are often written in simplified form:

$$\Psi(x_1, x_2 \dots x_n) = |\chi_1 \chi_2 \dots \chi_n\rangle \quad (76)$$

where the normalization is implied. Hartree-Fock uses a single Slater Determinant to determine the ground state energy. The variation principle states that any energy we find by adding and subtracting atomic orbitals will be an upper bound for the true energy of the configuration; that is, the best approximation to the molecular wave function is the one with the lowest energy. This can be done iteratively with the help of a software package. An initial guess at the linear combination of atomic spin orbitals that gives the Slater Determinant will give the average field term in the Fock operator. This Fock operator will have eigenfunctions which are Slater Determinants different from those initially guessed. These new combinations can be used to find a new average-field term

again, and so on until the eigenfunctions are consistent with the Fock operator. Because the object is to iteratively vary the Slater Determinants until the electric field calculated from them is consistent with the Fock operator whose eigenfunctions they are, this process is called self-consistent field, or SCF. This method is an approximation—but the more atomic orbitals that are used the lower the energy will be and the better the approximation.

### Configuration Interaction (CI) and MCSCF

The Configuration Interaction (CI) method is a refinement beyond Hartree-Fock that is considered a deeper level of theory by using multiple Slater Determinants rather than just one as in Hartree-Fock (Szabo, 1996:231-270). Given a complete set of spin orbitals,  $\chi_i(x_1)$ , one can construct any arbitrary function within the space:

$$\Phi(x_1) = \sum_i a_i \chi_i(x_1) \quad (77)$$

It can be shown as well for two variables:

$$\Phi(x_1, x_2) = \sum_{i,j} a_{i,j} \chi_i(x_1) \chi_j(x_2) \quad (78)$$

As before if this is a wave function we would like it to be antisymmetric, so we use a Slater Determinant instead:

$$\Phi(x_1, x_2) = \sum_{i < j} a_{i,j} |\chi_i \chi_j\rangle \quad (79)$$

And in general

$$\Phi(x_1, x_2 \dots x_n) = \sum_{i < j \dots n} a_{ij \dots n} |\chi_i \chi_j \dots \chi_n\rangle \quad (80)$$

Thus CI goes beyond Hartree-Fock by defining the wave function not only by the single



Slater Determinant giving the lowest energy, but as a linear combination of all possible Slater Determinants of  $n$  electrons. This yields a lower and thus more accurate energy for the configuration by the variation principle. If we define  $|\Phi_0\rangle$  as the Hartree-Fock ground state Slater Determinant, we can express other Slater Determinants as excitations out of this one. For instance, if  $|\Phi_0\rangle = |\chi_1 \dots \chi_i \dots \chi_n\rangle$  then we can create  $|\Phi_i^j\rangle = |\chi_1 \dots \chi_j \dots \chi_n\rangle$ , a singly excited determinant, by replacing the spin orbital  $\chi_i$  with  $\chi_j$ . We can also create and name doubly, triply, quadruply, et c. excited determinants and define the wave function as:

$$|\Psi\rangle = c_0 |\Phi_0\rangle + \sum_{ar} c_{ar} |\Phi_a^r\rangle + \sum_{a<b, r<s} c_{abrs} |\Phi_{ab}^{rs}\rangle + \dots \quad (81)$$

Once again we are limited by the fact that we do not have an infinite number of atomic orbitals with which to construct molecular wave functions, nor can we sum several multiply-excited determinants before we get bogged down. As in the Hartree-Fock method, a truncated basis of atomic orbitals must be chosen, and a limit on excited determinants must be chosen as well. Many software packages limit the sum to doubly excited determinants. Then the determinants as well as the coefficients are varied until a lowest upper bound is found for the energy. This process of optimization is called multiconfiguration self-consistent field, or MCSCF.

## Appendix C: *Columbus*' Calculation of the Derivative Coupling Term

Lischka et al. describe the method *Columbus* uses to calculate the NAD terms which, while more in depth, takes a similar form at least in part to the method used by Koppel (2004:7323). From CI we know that the electronic wave functions are linear combinations of other functions. In Appendix B they were referred to as various Slater Determinants. In the text of Lischka et al. the term configuration state function (CSF) is used (2004:7322). Thus the electronic wave functions take the form

$$|\varphi_i\rangle = \sum_n c_n^i |\psi_n\rangle \quad (82)$$

where  $\psi_n$  is the CSF. Substituting into the form of the NAD term we get:

$$P_{ij} \equiv \langle \varphi_i | \bar{\nabla} \varphi_j \rangle = \sum_n c_n^i \langle \psi_n | \bar{\nabla} \left( \sum_m c_m^j |\psi_m\rangle \right). \quad (83)$$

Thus the NAD term can be further broken down:

$$P_{ij} = \sum_n c_n^i \langle \psi_n | \sum_m \bar{\nabla} (c_m^j) |\psi_m\rangle + \sum_n c_n^i \langle \psi_n | \sum_m c_m^j | \bar{\nabla} \psi_m \rangle. \quad (84)$$

Since the  $\psi$ 's are orthonormal, the first term is just an inner product leaving only the coefficients so that

$$\sum_n c_n^i \langle \psi_n | \sum_m \bar{\nabla} (c_m^j) |\psi_m\rangle = \langle \bar{c}^i | \bar{\nabla} \bar{c}^j \rangle. \quad (85)$$

Lischka et al. use the same rationale as Koppel to rewrite this term as

$$\langle \bar{c}^i | \bar{\nabla} \bar{c}^j \rangle = \frac{\langle \bar{c}^i | \bar{\nabla} \hat{H} | \bar{c}^j \rangle}{E_j - E_i}. \quad (86)$$

Thus the NAD term can be written as two distinct terms:

$$P_{ij} = \frac{\langle \bar{c}^i | \bar{\nabla} \hat{H} | \bar{c}^j \rangle}{E_j - E_i} + \sum_{nm} c_n^i c_m^j \langle \psi_n | \bar{\nabla} \psi_m \rangle \quad (87)$$

the former being called the CI term and the latter the CSF term (Lischka 2004:7323).

This is how the NAD term is calculated in *Columbus* and most likely in *Brooklyn* as well.

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